A COURSE OF INSTRUCTION

IN THE

GENERAL PRINCIPLES

OF

CHEMISTRY

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CHAPTER I

THE COMPOSITION OF SUBSTANCES

1. Definition of the Field of Chemistry. Its General Principles the Subject of this Course.— *Chemistry* treats of the composition of substances, of their properties in relation to their composition, of changes in their composition, and of the effects attending such changes.

General chemistry, often called also theoretical or physical chemistry, treats of the general principles which have been found to express certain common characteristics of the numerous phenomena of chemistry. To a discussion of the more important of these general principles this Course will be devoted. The divisions of the subject will be taken up in the order in which they were named in the above-given definition of the field of chemistry.

2. Pure Substances and Mixtures, and the Law of Definite Proportions.— Out of the materials occurring in nature there can be prepared substances which, when subjected to suitable processes of *fractionation* (that is, to operations which resolve the materials into parts or fractions), always yield fractions whose properties are identical when measured at the same pressure and temperature. Such substances are called *pure substances;* other substances which can be resolved by such processes into fractions with different properties being called *mixtures.* For example, whether a solid material is a pure substance or mixture may be determined by partially melting or vaporizing it or by partially dissolving it in solvents, and by comparing the value of the density, melting-point, or some other sensitive property, of the unmelted, unvaporized, or undissolved part with that of the original material.

The fundamental idea involved in the preceding considerations is that there exists an order of substances, called pure substances, of relatively great stability toward resolving agencies, each one of which has a perfectly definite set of properties, sharply differentiated from those of other pure substances; so that there is not a continuous series of pure substances whose properties pass over into one another by insensible gradations.

1

This principle of definiteness of properties in general applies also to the elementary composition of pure substances. This fact is expressed by the *law of definite proportions,* which states that a pure substance, however it be prepared, always contains its elements in exactly the same proportions by weight.

3. The Law of Combining Weights.—To the various elements definite numerical values can be assigned which accurately express the weights of them, or small multiples of the weights of them, which are combined with one another in all pure substances. Such numerical values are called the *combining weights* of the elements. They are essentially relative quantities. Adopting 16 as the combining weight of oxygen, the *combining weight* of any other element may be defined to be that weight of it which combines with 16 parts of oxygen, or with some small multiple or submultiple of 16 parts of oxygen; and the above principle, known as the *law of combining weights,* can be expressed as follows: Elements are present in pure substances only in the proportions of their combining weights or of small multiples of them.

Prob. 1. The oxide of a certain element contains 30.06% of oxygen, and the sulphide of the same element contains 53.46% of sulphur. What does the law of combining weights show as to the relative weights of oxygen and sulphur that may be present in the pure compounds of these two elements?

4. Determination of Combining Weights.—The way in which some important combining weights have been determined is illustrated by the following problem.

Prob. 2. Determine the exact combining weights of silver, potassium, and chlorine from the following data: In a series of eight experiments 801.48 g. of pure potassium chlorate were ignited or treated with hydrochloric acid, yielding 485.66 g. of potassium chloride. In another series of five experiments 24.452 g. of pure potassium chloride were dissolved in water and precipitated with silver nitrate, whereby 47.013 g. of silver chloride were obtained. In a third series of ten experiments 82.669 g. of pure silver were dissolved in nitric acid and precipitated with hydrochloric acid, yielding 109.840 g. of silver chloride.

The combining weights adopted by the International Committee on Atomic Weights for the more important elements are presented in the following table, those multiples being given which have been shown to be the atomic weights, as described in Art. 17. The table is therefore also one of atomic weights.

Aluminum	. . . .	Al	27.1
Antimony	. . . .	Sb	120.2
Argon .	. . . . .	A	39.88
Arsenic	. . . .	As	74.96
Barium	. . . .	Ba	137.37
Beryllium	. . . .	Be	9.1
Bismuth .	. . . .	Bi	208.0
Boron .	. . . . .	B	11.0
Bromine .	. . . .	Br	79.92
Cadmium	. . . .	Cd	112.40
Calcium .	. . . .	Ca	40.07
Carbon	. . . . .	C	12.005
Chlorine .	. . . .	Cl	35.46
Chromium	. . . .	Cr	52.0
Cobalt .	. . . . .	Co	58.97
Copper	. . . . .	Cu	63.57
Fluorine .	. . . .	F	19.0
Gold .	. . . . .	Au	197.2
Helium	. . . . .	He	4.00
Hydrogen	. . . .	H	1.008
Iodine .	. . . . .	I	126.92

Iron	. . . . .	Fe	55.84
Lead	. . . . .	Pb	207.20
Lithium	. . . .	Li	6.94
Magnesium	. . . .	Mg	24.32
Manganese	. . . .	Mn	54.93
Mercury	. . . .	Hg	200.6
Nickel .	. . . .	Ni	58.68
Nitrogen .	. . . .	N	14.01
Oxygen	. . . .	O	16.00
Phosphorus	. . . .	P	31.04
Platinum .	. . . .	Pt	195.2
Potassium	. . . .	K	39.10
Radium	. . . .	Ra	226.0
Silicon	. . . .	Si	28.3
Silver .	. . . . .	Ag	107.88
Sodium	. . . .	Na	23.00
Strontium	. . . .	Sr	87.63
Sulphur	. . . .	S	32.06
Thallium .	. . . .	Tl	204.0
Tin .	. . . . .	Sn	118.7
Zinc	. . . . .	Zn	65.37

5. The Atomic and Molecular Theories account for the fact that elements combine with one another only in the proportions of their combining weights or small multiples of them by assuming that any mass of each element is made up of a very large number of extremely small particles called *atoms;* that these are exactly alike in every respect; that they are not subdivided by chemical processes; that there are as many kinds of atoms as there are elements; that the atoms associate with one another, usually in small numbers, forming a new order of distinct particles called *molecules;* that pure chemical substances are made up of only one kind of molecules, while mixtures contain two or more kinds; and that the molecules of elementary substances consist of atoms of the same kind, those of compound substances of atoms of different kinds.

These assumptions in regard to atoms and molecules have now been confirmed in so many ways that they are no longer hypothetical.

By the above statement *chemical substances* are implicitly defined from the molecular standpoint as pure substances which contain only a single kind of molecule. Thus, the pure substance liquid water contains the two chemical substances whose molecules are H_2O and H_4O_2, these being always present in definite proportions at any definite temperature

and pressure, since equilibrium is instantaneously established between them; but the pure substance water-vapor, which contains only molecules of the form H_2O, is a single chemical substance. Pure substances which, like water, water-vapor, and ice, are converted into each other by changes of pressure and temperature, are commonly spoken of as the same substance; but they may consist of different chemical substances, as has been just illustrated.

The relative weights of the atoms of the various elements and of the molecules of the various substances are called their *atomic weights* and *molecular weights,* respectively; and as a standard of reference, the weight of the oxygen atom taken as 16 is adopted.

The atomic theory evidently requires that the weights of elements that combine with one another be proportional to the weights of their atoms or to small multiples of those weights; in other words, that the atomic weights be equal to the combining weights or to small multiples of them. Which multiple of the combining weight is the atomic weight cannot be derived from the elementary composition of substances. It can, however, be derived from other properties, with the aid of certain other principles.

6. Chemical Formulas, Formula-Weights, and Equivalent-Weights.
—In order to express the gravimetric composition of compounds, the symbols of the elements are considered to represent their atomic weights and are written in sequence with such integers as subscripts as will make the resulting formula express the proportions by weight of the elements in the compound.

The formula is commonly so written as to represent also the number of atoms of each element present in the molecule, when this has been determined (by any of the methods described in later articles).

The formula represents, in addition, a definite weight of the substance, namely, the weight in grams which is equal to the sum of the numbers represented by the symbols of the elements in the formulas. This weight is called the *formula-weight* of the substance. Thus the formula HNO_3 denotes $1.008 + 14.01 + (3 \times 16.00)$ or 63.02 grams of nitric acid.

Those weights of various substances which enter into chemical reactions with one another are called equivalent weights. Adopting one formula-weight or 1.008 grams of the element hydrogen as the

standard of reference, the *equivalent-weight* or *one equivalent* of any substance is defined to be that weight of it which reacts with this standard weight of hydrogen, or with that weight of any other substance which itself reacts with this standard weight of hydrogen. Thus the equivalent-weight of each of the following substances is that fraction of its formula-weight which is indicated by the coefficient preceding the formula: $\frac{1}{2}Cl_2$; $\frac{1}{4}O_2$; $1Ag$; $\frac{1}{2}Zn$; $\frac{1}{3}Bi$; $1NaOH$; $\frac{1}{2}Ba(OH)_2$; $\frac{1}{2}H_2SO_4$; $\frac{1}{3}H_3PO_4$; $\frac{1}{3}AlCl_3$; $\frac{1}{4}K_4Fe(CN)_6$. The equivalent-weight of a substance may have different values depending on whether it is considered with reference to a reaction of metathesis or to one of oxidation and reduction. Thus, the metathetical equivalent of ferric chloride is $\frac{1}{3}FeCl_3$ but its oxidation-equivalent (with respect to its conversion to ferrous chloride) is $1FeCl_3$; the metathetical equivalent of potassium chlorate is $1KClO_3$, but its oxidation-equivalent (with reference to its reduction to KCl) is $\frac{1}{6}KClO_3$.

CHAPTER II

PROPERTIES OF GASES RELATED TO MOLECULAR COMPOSITION

PRESSURE–VOLUME RELATIONS OF GASES

7. The Laws of Perfect Gases are the limiting laws to which gases conform more and more closely as their pressure approaches zero. These laws express fairly closely (within less than one percent) the behavior of gases up to pressures not much greater than one atmosphere, provided they are far removed from their temperatures of condensation.

8. Boyle's Law.—At any definite temperature the pressure p of a definite weight m of any perfect gas is inversely proportional to its volume v. Or, since *density d* is defined to be the ratio m/v of the weight of a substance to its volume, the pressure of any perfect gas at any definite temperature is directly proportional to its density.

9. Gay-Lussac's Law of Temperature-Effect.—When different perfect gases are heated or cooled from a definite initial to a definite final temperature, their pressure-volume products $p\,v$ change by the same fractional amount.

This principle and its degree of accuracy when applied to gases at moderate pressures are illustrated by the following data: When 1000 ccm. of gas at 0° and a pressure of 1000 mm. of mercury are heated to 100° at constant pressure, the volume increases by 367 ccm. with nitrogen, 366 ccm. with hydrogen, and 374 ccm. with carbon dioxide; when heated at constant volume, the pressure increases by 367, 366, and 373 mm., with the three gases, respectively.

10. Definition of Absolute Temperature.—Absolute temperature T is so defined that the pressure-volume product $p\,v$ of a perfect gas is directly proportional to it. Since the pressure-volume product decreases $\frac{1}{273.1}$ of its value at 0° for each degree that the temperature decreases, the absolute zero is at —273.1°; and the absolute temperature T is equal to $t + 273.1$ (approximately **273***), where t is the ordinary centigrade temperature.

*Approximate values of numerical constants which it is well to remember are printed in black-face type. These values will be given so as to be accurate to 0.1%.

11. Expression of the Physical Laws of Perfect Gases.—The laws of Boyle and Gay-Lussac, the definition of absolute temperature, and the obvious proportionality between the value of the pressure-volume product and the weight m of the gas are all expressed by the equation $pv = m \overline{R} T$, in which $\overline{R}$ is a constant, evidently representing the value of pv/T for one gram of the gas, which has different values for different gases.

Prob. 1. From the fact that the density of oxygen is 0.001429 g. per ccm. at 0° and 1 atm. calculate the volume in liters of 32 g. of it at 20° and 1 atm.

12. Law of Combining Volumes and the Principle of Avogadro.— The foregoing physical laws acquire an important chemical significance by reason of the *law of combining volumes,* which may be stated as follows : Those quantities of perfect gases that are involved in chemical reactions with one another have at the same temperature and pressure volumes which are equal or small multiples of one another. Thus the quantities of hydrogen and of oxygen which unite with each other to form water have volumes whose ratio approaches the exact value 2 :1 as the pressure of the gases approaches zero. In other words, those quantities of different substances which as perfect gases have the same value of the product pv/T are equal to, or are small multiples of, the quantities which are involved in chemical reactions with one another. Now, since according to the molecular theory substances react by molecules, these quantities of different perfect gases which have the same value of pv/T must contain either an equal number of molecules or small multiples of an equal number.

These considerations suggest a simpler hypothesis, known as the *principle of Avogadro,* which may be stated as follows : Those quantities of any perfect gases which have the same volume at the same temperature and pressure, and therefore the same value of pv/T at any temperature and pressure, contain an *equal* number of molecules.

This principle, originally hypothetical, has now been so fully verified that it has become one of the fundamental laws of chemistry.

Prob. 2. From the principle of Avogadro show that the densities of perfect gases at the same temperature and pressure are proportional to their molecular weights.

13. Empirical Definition of Molecular Weight and of Mol.—The principle of Avogadro evidently enables the relative weights of the

molecules of different gaseous substances to be determined. To express these relative weights more definitely, the ratio of the weight of the molecule of any substance to the weight of the molecule of oxygen taken as 32 is commonly considered, this ratio being called the *molecular weight M* of the substance. The number 32 is adopted as the reference quantity of oxygen, since (as shown in Prob. 13) it corresponds to the adoption of 16 as the atomic weight of oxygen.

The so-defined molecular weight of a substance may evidently be experimentally determined by finding the number of grams of it which have that value of pv/T which 32 grams of oxygen have, when both substances are in the state of perfect gases. This number of grams is called *one mol* of the substance—a unit-quantity* which has great importance in chemical considerations, both because it is directly related to molecular weight and because it makes possible a general expression of the laws of perfect gases, as shown in the following Article.

14. General Expression of the Laws of Perfect Gases.—Representing by R the constant value of pv/T for one mol and by N the number of mols of the gas present, the laws of perfect gases may be expressed in a general form by the following equation, hereafter called the *perfect-gas equation:*

$$p \; v = N \; R \; T.$$

The numerical value of the *gas-constant R* depends on the units in which the pressure, volume, and temperature are expressed. In scientific work, temperature is always expressed in centigrade degrees (here on the absolute scale); volume is ordinarily expressed in cubic centimeters or liters; and pressure in dynes per square centimeter, millimeters of mercury, or atmospheres. One *dyne* is a force of such magnitude that when it acts on a freely moving mass of one gram it increases its velocity each second by one centimeter per second; and the pressure of one dyne per square centimeter is called one *bar,* 10^6 bars being called one *megabar.*† One *atmosphere* is a pressure equal to that exerted by a column of mercury 76 cm. in height at 0° at the sea-level in a latitude of 45°. The value of the gas-constant R when

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*This unit-quantity is called by some authors one gram-molecular weight or one gram-molecule of the substance.

† The megabar is a unit of the same general magnitude as the atmosphere, and should replace it in scientific work; but unfortunately it is not yet generally employed.

the pressure is in atmospheres and the volume is in cubic centimeters is 82.07 (approximately **82**).

Prob. 3. Calculate the value of the atmosphere in dynes per sq. cm. and in megabars. The density of mercury at 0° is **13.60**. The force of gravity acting on any freely moving body increases its velocity each second by g centimeters per second. The value of g at the sea-level in a latitude of 45° is 980.6 (approximately **980**) centimeters per second.

Prob. 4. Calculate precisely the value of the gas-constant R when the pressure is in atmospheres and the volume in cubic centimeters, from the fact that one gram of oxygen has at 0° and 0.1 atm. a volume of 7005 ccm. Assume in this problem and the following ones that the substance behaves as a perfect gas.

Prob. 5. Seven grams of a certain gas have a volume of 6.35 l. at 20° and 720 mm. How many grams make one mol?

Prob. 6. What is the volume occupied by 12 g. of ether vapor ($C_4H_{10}O$) at 80° and 600 mm.? What is the density? What is the ratio of the density to that of oxygen at the same temperature and pressure?

Prob. 7. How many grams of iron must be taken to produce by its action on sulphuric acid one liter of hydrogen (H_2) at 27° and 1 atm.?

15. Dalton's Law of Partial Pressures.—In a mixture of perfect gases each chemical substance (defined as in Art. 5 to be a substance consisting of a particular kind of molecule) has the same pressure as it would if it were alone present in the volume occupied by the mixture. The pressures of the separate substances are called *partial pressures*.

Partial pressures have been experimentally determined in certain cases. Thus, when a platinum vessel containing a mixture of hydrogen and nitrogen at a high temperature is immersed in an atmosphere of hydrogen, hydrogen passes through the platinum walls until its pressures within and without the vessel become equal; the difference then observed between the total pressure of the mixture within the vessel and the pressure of the hydrogen outside is due to the nitrogen, which does not pass through the wall; and this difference is equal to its partial pressure. Walls of this kind, permeable for only one of the substances present in a mixture, are called *semipermeable walls*.

The principal evidence in support of Dalton's law is, however, the fact that the total pressure of a mixture of perfect gases is actually equal to the sum of the partial pressures calculated by the law.

By the *molal composition* of a mixture is meant its composition expressed in terms of the number of mols of each of the substances.

The ratio of the number of mols of any one substance to the total number of mols in the mixture is called the *mol-fraction x* of that substance; that is, $x_1 = N_1/(N_1 + N_2 + ..)$. The partial pressure of each substance in a mixture of perfect gases is evidently equal to the product of its mol-fraction by the total pressure of the mixture.

Pure dry air contains 21.0 mol-percent of oxygen (O_2), 78.1 mol-percent of nitrogen (N_2), and 0.9 mol-percent of argon (A). The corresponding value of one mol of air is 29.00 grams, in agreement with the value directly derived from density measurements. With the aid of this value the perfect-gas equation may be applied directly to air.

Prob. 8. a. From the composition of air given above, calculate the partial pressures of the separate substances in millimeters of mercury when the barometer stands at 1 atm. *b.* Calculate the number of grams which make one mol of air. *c.* Calculate the percent by weight of oxygen in air.

Prob. 9. A Bessemer converter is charged with 10,000 kilos of iron containing 3% carbon. How many cubic meters of air at 27° and 1 atm. are needed for the combustion of all the carbon, assuming one-third to burn to CO_2 and two-thirds to CO? What are the partial pressures of the gases evolved?

Prob. 10. At 50° and 500 mm., nitrogen tetroxide has a density 2.15 times that of air under the same conditions. What percentage dissociation according to the equation $N_2O_4 = 2NO_2$ must be assumed to explain this value? What is the partial pressure of each gas (NO_2 and N_2O_4) in the mixture?

16. Determination of Molecular Weights.—The experimental determination of the molecular weight of a gaseous substance consists in measuring the volume of a weighed quantity of the substance at an observed pressure and temperature. From these quantities ($v, m, p,$ and T) the molecular weight of the substance is calculated with the aid of the perfect-gas equation.

Prob. 11. Determination of Vapor-Density by Hofmann's Method.— 0.1035 g. of a volatile liquid is introduced into the vacuum above a mercury column in a graduated tube standing in an open vessel of mercury. The tube is entirely surrounded by a jacket through which steam at 100° is passed. The mercury column falls till it stands 260 mm. above the mercury-level in the vessel below, and the volume of the completely vaporized liquid is observed to be 63.0 ccm. The barometric pressure at the time is 752 mm. At 100° the density of mercury is 13.35, and its vapor-pressure is negligible. Calculate the density and the molecular weight of the vapor.

Since gases at atmospheric pressure conform to the perfect-gas laws only approximately, and since gaseous densities are not commonly determined with so great accuracy as the composition of substances, the exact value of the molecular weight of a compound is usually derived from the analytical data, the density being employed only to determine what multiple or submultiple of the value so derived is in accordance with Avogadro's principle.

Prob. 12. *a.* A certain oxide contains exactly 72.73% of oxygen. What does this show in regard to its molecular weight? *b.* At 0° and 1 atm., one liter of this (gaseous) oxide is found to weigh exactly 1.977 g. What is the molecular weight of the oxide corresponding to this datum? *c.* What is the exact molecular weight derived by considering the data relating both to the composition and density? *d.* What do these two values of the molecular weight show as to the percentage deviation of the density from that required by the perfect-gas equation?

17. Derivation of the Atomic Weights of Elements and of the Molecular Composition of Compounds.— The exact values of atomic weights are based on analytical determinations of the combining weights, as described in Art. 4. The multiple of the combining weight adopted as the *atomic weight* of any element is derived by finding the smallest weight of the element contained in one molecular weight of any of its gaseous compounds. This is the true atomic weight only in case some one of the compounds studied contains in its molecule a single atom of the element; and the adopted atomic weight is therefore strictly only a maximum value, of which the true atomic weight may be a submultiple. The probability that the true atomic weight has been found evidently increases with the number of the gaseous compounds whose molecular weights have been determined.

The multiples of the combining weights adopted as the atomic weights have, however, not been derived solely from molecular-weight determinations. From the laws relating to certain other properties, such as the heat-capacities of gaseous and solid substances (considered in Arts. 118 and 120), independent values of the atomic weights have been obtained, which confirm and extend those derived from molecular weights.

The *molecular composition* of a gaseous substance (that is, the number and nature of the atoms in its molecule) can evidently be derived from its molecular weight, its composition by weight, and the atomic weights of the elements contained in it. The chemical formulas

of substances whose molecular weights in the gaseous state are known are ordinarily so written as to express this molecular composition. Such formulas are called *molecular formulas.*

Prob. 13. Certain oxygen compounds have molecular weights M (referred to that of oxygen as 32) and percentages of oxygen x as follows: Sulphur trioxide, $M = 80.07$, $x = 59.95$; water, $M = 18.02$, $x = 88.80$; carbon dioxide, $M = 44.00$, $x = 72.73$. *a.* Find the weight of oxygen contained in one molecular weight of each of these oxides. *b.* State how these values show that the atomic weight of the element oxygen is one-half of the assumed molecular weight of oxygen gas, and therefore that the molecule of oxygen gas consists of two atoms.

Prob. 14. a. Calculate the combining weight of the element contained in the oxide whose composition was given in Prob. 12*a. b.* What conclusion as to its atomic weight can be drawn from this combining weight and the density given in Prob. 12*b*? *c.* What conclusion can be drawn as to the molecular formula of the oxide?

Prob. 15. a. The chloride of a certain element is found by analysis to contain 52.50% Cl, whose atomic weight is 35.46; and it is found to have at 150° a vapor-density 4.71 as great as that of air. What conclusion can be drawn from these facts as to the exact atomic weight of the element? *b.* The hydride of the same element is a gas which contains 5.91% of hydrogen; and it is found to be produced without change in volume when hydrogen (H_2), whose atomic weight is 1.008, is passed over the solid elementary substance. What conclusion can now be drawn as to the atomic weight of the element? *c.* What are the simplest molecular formulas of the hydride and of the chloride consistent with these conclusions?

Prob. 16. A certain hydrocarbon is composed of 92.25% of carbon and 7.75% of hydrogen, whose atomic weights are 12.00 and 1.008, respectively. Its density in the form of vapor at 100° and 1 atmosphere is 2.47 times as great as that of oxygen under the same conditions. Calculate its exact molecular weight, and derive its molecular formula.

The molecules of elementary substances may consist of single atoms or of two or more atoms. Thus the molecular formulas of some of those whose density in the gaseous state has been determined are: H_2, N_2, O_2, F_2, Cl_2, Br_2, I_2, P_4, As_4, He, A, Hg, Cd, Zn. At very high temperatures some of these have been shown to dissociate into simpler molecules; thus above 1500° the molecule of iodine consists of a single atom.

A knowledge of the molecular formulas of substances is of importance principally because the chemical relationships of different substances are far more clearly brought out by such formulas than by the simpler ones expressing merely composition by weight. The

structure theory, which underlies the science of organic chemistry, is based upon a knowledge of the molecular weights of substances.

18. Deviations from the Perfect-Gas Laws at Moderate Pressures.

Prob. 17. Calculate accurately the percentage deviations at 0° and 1 atm. of the volumes of one mol of oxygen and of one mol of nitrous oxide from that of a perfect gas. At 0° and 1 atm. the density of oxygen is 0.001429, and that of nitrous oxide (N_2O) is 0.001978.

The deviations from the perfect-gas law, so long as they do not exceed a few percent, are accurately expressed by the equation $p v = N R T (1 + \alpha p)$, in which α is an empirical coefficient which can be determined for each gas at each temperature from a measurement of $p v$ at some one pressure. The following table shows the values of 100α, representing the percentage deviation of $p v$ from $N R T$ at one atmosphere, for various gases at 0°, together with their condensation-temperatures.

Formula of gas...	He	H_2	N_2	NO	CO_2	NH_3	SO_2
100α	+0.06	+0.05	−0.04	−0.12	−0.68	−1.52	−2.38
Condensation-temp.	−269°	−253°	−196°	−151°	−78°	−34°	−10°

19. Pressure-Volume Relations of Gases at High Pressures.—In Figure 1 are plotted the values of $p v/T$ (in arbitrary units) as ordi-
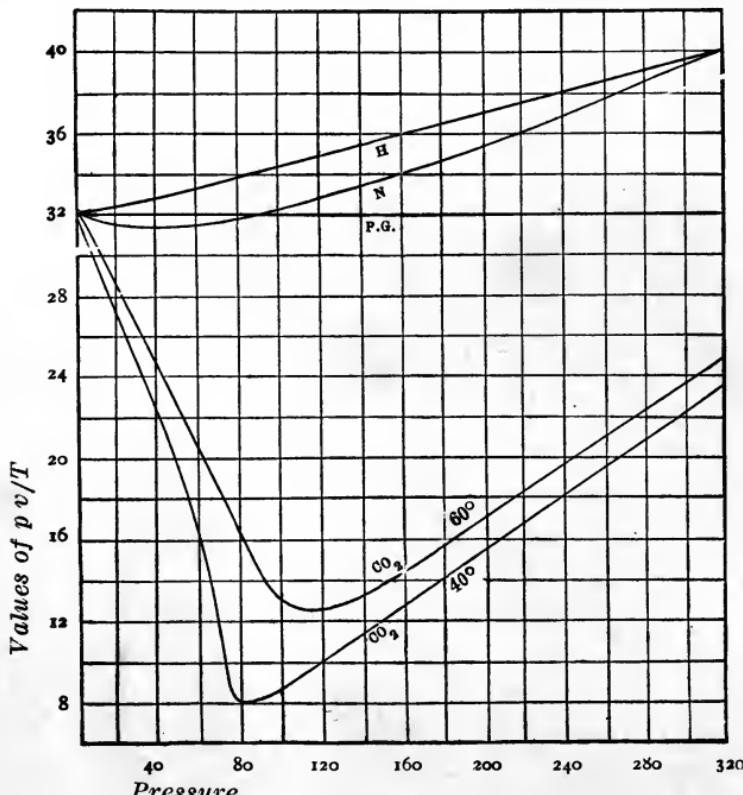

FIGURE 1

nates against the values of the pressure (in meters of mercury) as abscissas for one mol of hydrogen at 60°, of nitrogen at 60°, of carbon dioxide at 60° and at 40°, and of a perfect gas (marked P. G. in the figure). At temperatures between 0° and 60°, helium (He) and neon (Ne) have curves similar to that of hydrogen (H_2); oxygen (O_2), carbon monoxide (CO), and nitric oxide (NO) have curves similar to that of nitrogen; and nitrous oxide (N_2O), ammonia (NH_3), and ethylene (C_2H_4) have curves similar to those of carbon dioxide (CO_2).

Prob. 18. Summarize the general conclusions in regard to the pressure-volume relations of gases that can be drawn from the curves of Figure 1, the statements in the preceding text, and the condensation-temperatures given in Art. 18.

Prob. 19. Estimate with the aid of the figure the ratio of the volume of one mol of each of the gases at 40 m. (or 53 atm.) to that which one mol of a perfect gas would have at the same temperature and pressure.

PROPERTIES OF SOLUTIONS RELATED TO MOLECULAR COMPOSITION

VAPOR-PRESSURE AND BOILING-POINT IN GENERAL

20. Vapor-Pressure.—A liquid in contact with a vacuous space vaporizes until the pressure of its vapor in that space attains a perfectly definite value which is determined by the nature of the liquid and by the temperature. If, on the other hand, vapor having a pressure greater than this definite value is brought into contact with the liquid, condensation occurs until the pressure of the vapor falls to that value. In other words, for a given liquid at a given temperature there is only one pressure which its vapor can have and exist in equilibrium with that liquid. This pressure is called the *vapor-pressure* of the liquid. This is to be distinguished from the pressure of the vapor, which when not in contact with the liquid may have any value from zero up to one somewhat exceeding the vapor-pressure. Solids likewise have definite vapor-pressures, which with certain substances (like iodine) are appreciable even at room temperature.

The vapor-pressure of a liquid or solid substance increases rapidly with increasing temperature, as illustrated by the data of Prob. 3 below.

When a liquid is in contact with a space containing a gas (for example, when water is in contact with an air space), approximately the same quantity of the liquid vaporizes as if the gas were not present, provided the gas is only slightly soluble in the liquid, and provided its pressure is not much greater than one atmosphere. When the gas is readily soluble in the liquid, or when its pressure is large, considerable deviations from this principle may result.

Prob. 1. At 28° and 1 atm. 25 ccm. of dry air are collected over water, whose vapor-pressure at 28° is 28 mm. *a.* What is the pressure if the volume is still 25 ccm.? *b.* What is the volume if the pressure is still 1 atm.?

Prob. 2.—Air-Bubbling Method of Determining Vapor-Pressure.— 2000 ccm. of dry air at 15° and 760 mm. are bubbled through bulbs containing a known weight of carbon bisulphide (CS_2) at 15°, and the mix-

ture of air and bisulphide vapor is allowed to escape into the air at a pressure of 760 mm. By reweighing the bulbs, 3.011 g. of the bisulphide are found to have vaporized. What is the vapor-pressure of carbon bisulphide at 15°?

Steam-Distillation of Liquids Insoluble in Water.—

Prob. 3. Steam is bubbled through chlorbenzene (C_6H_5Cl) in a distilling flask; and the vapors, which escape under a barometric pressure of 1 atm., are condensed as a distillate. The steam partially condenses in the distilling flask, and brings the mixture of water and chlorbenzene (which are not appreciably soluble in one another) to that temperature where equilibrium prevails between each liquid and its vapor. Determine this temperature and the molal composition of the distillate with the aid of a plot of the following data, which represent the vapor-pressures of the pure substances at various temperatures:

	70°	80°	90°	100°
Water	234	355	526	760 mm.
Chlorbenzene . . .	98	145	208	292 mm.

Prob. 4. A current of steam is passed at atmospheric pressure through a mixture of water and nitrobenzene ($C_6H_5NO_2$). Calculate the temperature of the distilling mixture and the percentage by weight of nitrobenzene in the distillate from the following data: the vapor-pressure of water at 100° is 760 mm. and changes by 3.58% per degree; that of nitrobenzene at 100° is 20.9 mm. and changes by 5.0% per degree.

21. Relation of Boiling-Point to Vapor-Pressure.—The *boiling-point* of a liquid is the temperature at which it is in equilibrium with its vapor when both are subjected to any definite external pressure. In other words, it is the temperature at which the vapor-pressure, which increases as the temperature rises, becomes equal to the external pressure. When this temperature is exceeded by an infinitesimal amount, assuming that there is no superheating, the vapor forms throughout the mass of the liquid (not merely at its free surface), giving rise to the familiar phenomenon of boiling.

Prob. 5. The vapor-pressure of water at 100° increases 27.2 mm. per degree. What variation of its boiling-point corresponds to a variation of the barometric pressure from 730 to 790 mm.?

22. Change of Vapor-Pressure with Temperature. The Clapeyron Equation.—From the laws of thermodynamics it can be shown that the rate at which the vapor-pressure p of a liquid or solid at the absolute temperature T increases with the temperature is expressed exactly by the *Clapeyron equation*:

$$\frac{dp}{dT} = \frac{\Delta H}{(v - v_0)T}$$

In this equation v represents the volume of one mol of the (saturated) vapor at the pressure p and temperature T, v_0 is the volume of one mol of the liquid or solid substance under the same conditions, and ΔH is the increase in the heat-content of the substance, equal to the heat withdrawn from the surroundings, when one mol of it vaporizes at the temperature T. The quantity ΔH is called the *molal heat of vaporization.*

Since at the boiling-point of a liquid its vapor-pressure is equal to the external pressure upon the liquid and vapor, the Clapeyron equation also expresses (more clearly in the inverted form) the change of boiling-point with the external pressure.

In numerical applications of this equation, the energy quantities ΔH and $(v - v_0)dp$ must be expressed in corresponding units. The latter quantity will be in ergs when the volumes are in cubic centimeters and the pressure is in dynes per square centimeter.

Three units of energy are commonly used in scientific work—the erg, the joule, and the calorie. The *erg* is the work done when a force of one dyne is displaced through one centimeter. The *joule* is a decimal multiple of the erg; namely, one joule equals 10^7 ergs. The *mean calorie* is one one-hundredth part of the heat required to raise one gram of water from $0°$ to $100°$. This is identical within 0.02% with the *ordinary calorie,* which is the heat required to raise one gram of water from $15°$ to $16°$. One calorie (1 cal.) is equal to 4.182 (approximately 4.18) $\times 10^7$ ergs, this value being the so-called mechanical equivalent of heat.

Prob. 6. a. Calculate with the aid of the Clapeyron equation the volume of one mol of saturated water-vapor at $100°$ from the following data: At $100°$ the vapor-pressure of water increases 27.2 mm. per degree, the heat of vaporization of one gram of it is 537 cal., and the specific volume (*i. e.,* the volume of one gram) of liquid water is 1.043. *b.* Calculate by the perfect-gas equation the volume of one mol of saturated water-vapor at $100°$. *c.* By comparing the two values of this quantity obtained in *a* and *b,* determine the percentage error made in assuming that the saturated vapor conforms to the perfect-gas law.

Note.—The molal volume of the vapor of alcohol saturated at $78.3°$ (where the pressure is 760 mm.) is 3.6% smaller, and that of the vapor of ether saturated at $12.9°$ (where the pressure is 330 mm.) is 3.5% smaller, than the molal volume calculated by the perfect-gas equation.

Prob. 7. a. Derive from the Clapeyron equation the simpler, but less exact, expression $\dfrac{d \log p}{d T} = \dfrac{\Delta H}{R T^2}$ by assuming that the volume of

the liquid is negligible in comparison with that of the vapor and that the vapor conforms to the perfect-gas laws. *b.* What percentage error in dp/dT would result from each of these assumptions if it be calculated for water at 100° by this approximate equation with the aid of the data of Prob. 6*a*? *c.* In numerical applications of this equation R and ΔH must be expressed in corresponding units. Show from the data of Prob. 4, Art. 14, that the value of R is 8.316 (approximately **8.32**) in joules per degree, and 1.9885 (approximately **1.99**) in calories per degree.

Prob. 8. a. Integrate the approximate Clapeyron equation so as to obtain a relation between the vapor-pressures p_1 and p_2 at two different temperatures T_1 and T_2. Assume that the heat of vaporization does not vary between the two temperatures. *b.* Calculate by the equation so obtained the boiling-point of water at 92 mm., and its vapor-pressure at 75°. Compare these calculated values with the actual ones given above. *c.* State what inexact assumptions are involved in the equation which would account for the divergence.

23. Solutions.—A *solution* is a physically homogeneous mixture of two or more chemical substances; that is, one which has no larger aggregates than the molecules themselves. Solutions thus defined may be gaseous, liquid, or solid; but only liquid solutions will be here considered. When one substance is present in large proportion it is called the *solvent,* and any substance present in small proportion is called a *solute.*

The composition of solutions is often expressed in terms of the mol-fractions of the substances, defined as in Art. 15.

In considering the equilibrium of solutions with the vapor or with the solid solvent, the term phase is conveniently employed. The *phases* of a system are its physically homogeneous parts, separated from one another by physical boundaries. Thus any gaseous mixture or any solution or any solid substance forms a single phase. A system may consist of any number of such phases. Thus a solution in contact with its vapor, or with the solid solvent, or with the solid solute, is an example of a two-phase system. A solution in contact both with the vapor and the solid solvent is a three-phase system.

With reference to the proportions in which the substances are present, two groups of solutions may be distinguished: *dilute solutions,* those in which the mol-fraction of the solute is small (not greater than 0.01 or 0.02); and *concentrated solutions,* those in which each substance is present in considerable proportion. There is, of course, no sharp line of demarcation between these two groups of solutions.

Some types of concentrated solutions and all dilute solutions conform approximately—more closely as the mol-fraction of the solute approaches zero—to certain laws, which, in analogy with the laws of perfect gases, may be called the *laws of perfect solutions.* The fundamental laws of perfect solutions are the vapor-pressure laws of Raoult and Henry, and the corresponding laws of distribution between phases and of the osmotic pressure of solutions. To consideration of these laws the rest of this chapter is mainly devoted.

VAPOR–PRESSURE AND BOILING–POINT OF DILUTE SOLUTIONS

24. Raoult's Law of Vapor-Pressure Lowering.—The addition of a solute to a solvent causes at any temperature a fractional lowering of the vapor-pressure of the solvent equal to the mol-fraction (x) of the solute. That is:

$$\frac{p_0 - p}{p_0} = \frac{N}{N_0 + N} = x,$$

where p_0 is the vapor-pressure of the pure solvent and p is its vapor-pressure above a solution consisting of N mols of solute and N_0 mols of solvent.* In this expression N_0 is equal to the weight m_0 of the solvent divided by its molecular weight M_0 in the *vapor,* and N is equal to the weight m of the solute divided by its molecular weight M in the *solution.* The value of M_0 is ordinarily that corresponding to the molecular formula of the solvent; for, as stated in Art. 9, the molecular formula is commonly so written as to represent the molecular weight of the substance in the state of a perfect gas.

In the case of very dilute solutions the mol-fraction $N/(N_0 + N)$ may evidently be replaced by the mol-ratio N/N_0, without causing appreciable error.

When the solute is so volatile as to have an appreciable vapor pressure, the quantity p in the Raoult equation denotes, of course, the partial vapor-pressure of the solvent, not the total vapor-pressure of the solution.

Although Raoult's law is exact only in the case of very dilute solutions, it holds true approximately up to moderate concentrations in all cases, and up to very high concentrations in some cases, as will be described in Art. 30.

*Throughout this chapter quantities referring to the solvent are represented by letters with the subscript zero, those referring to the solution or solute by letters without subscripts.

Determination of Molecular Weights and Molecular Composition.—

Prob. 9. At 30° the vapor-pressure of ethyl alcohol (C_2H_5OH) is 78.0 mm., and that of an alcohol solution containing 5% of a non-volatile substance is 75.0 mm. What is the molecular weight of the substance?

Prob. 10. The experiment described in Prob. 2, Art. 20, was repeated, using in place of pure carbon bisulphide an 8.00% solution of sulphur in carbon bisulphide. 2.902 g. of carbon bisulphide were found to have vaporized. Calculate the molecular weight of the sulphur, and find its molecular formula.

Raoult's law may also be stated in the following simple form, which indicates more clearly its real significance: the vapor-pressure (p) of the solvent in a perfect solution is proportional to its mol-fraction (x_0); that is, representing by p_0 the vapor-pressure of the pure solvent,

$$p = p_0 \, x_0.$$

Prob. 11. *a.* Show that the two statements of Raoult's law are mathematically equivalent. *b.* Show that the second statement of the law requires that the proportionality-factor be the vapor-pressure of the pure solvent, as is assumed in the mathematical expression of it.

Raoult's law relates fundamentally to the distribution between the liquid phase and vapor phase of the chemical substance (Art. 5) whose partial pressure in the vapor is under consideration. In other words, from the molecular standpoint, it relates to the distribution of the kind of molecules which give rise to this partial pressure. It shows that the number of these molecules which are present in unit-volume of the vapor when equilibrium has been reached is proportional to the ratio in the liquid of the number of this kind of molecule to the total number of molecules of all kinds. Moreover, since this molecule-ratio is unity for a solvent which consists solely of the kind of molecule under consideration, the proportionality-factor in the expression of the law is the vapor-pressure of the pure solvent.

Raoult's law in the forms considered above presupposes that the vapor conforms to the perfect-gas law. It can be shown that the deviation of the vapor from this law, when expressed (as in Art. 18) by the equation $p\,v = R\,T\,(1 + a\,p)$, can be substantially corrected for, so long as neither the mol-fraction of the solute nor the correction term $\propto p_0$ exceeds 5 percent, by writing the Raoult equation in the form:

$$p\,(1 + \propto p) = x_0 p_0\,(1 + \propto p_0).$$

25. Relation of Boiling-Point Raising to Vapor-Pressure Lowering for Non-Volatile Solutes.

Prob. 12. *a.* What is the vapor-pressure in mm. of a solution at 100° containing 5 g. of glucose ($C_6H_{12}O_6$) in 100 g. of water? *b.* What is its boiling-point? Its vapor-pressure at 100°, like that of water, increases 3.58% per degree.

Prob. 13. The vapor-pressure of ethyl alcohol is 721.5 mm. at 77°, 751.0 at 78°, 781.5 at 79°, and 813.0 at 80°. *a.* Plot on a large scale these vapor-pressures as ordinates and the temperatures as abscissas. Calculate the vapor-pressures at 78, 79, and 80° of a solution consisting of 2 mols of a solute and 98 mols of alcohol, and of one consisting of 4 mols of solute and 96 mols of alcohol; and plot these values on the diagram. *b.* With the aid of the diagram find the boiling-points at 1 atm. of pure alcohol and of the two solutions. *c.* Show from the geometrical relations of the diagram that the raising of the boiling-point is proportional to the lowering of the vapor-pressure at the boiling-point of the solvent, for dilute solutions (for which the graphs may be considered to be parallel straight lines). *d.* Find the value for ethyl alcohol of the proportionality-constant involved in the relation just stated.

Representing by $T - T_0$ the raising of the boiling-point and by $p_0 - p$ the lowering of the vapor-pressure produced by increasing the mol-fraction of the solute from 0 to x, and representing by dT_0/dp_0 the reciprocal of the rate of change of the vapor-pressure of the solvent with the temperature, the relations derived in the preceding problem for dilute solutions may be expressed by the equation:

$$T - T_0 = \frac{dT_0}{dp_0}(p_0 - p).$$

26. Relation between Boiling-Point Raising and Molal Composition.

—By combining the expression derived in the preceding article with Raoult's equation for vapor-pressure lowering there is obtained the following relation between the raising of the boiling-point ($T - T_0$) and the mol-fraction x of the solute:

$$T - T_0 = \left(\frac{dT_0}{dp_0/p_0}\right) x.$$

The quantity $\dfrac{dT_0}{dp_0/p_0}$ is evidently a constant characteristic of the solvent, which may be called its *boiling-point constant*. Another expression for it, in terms of the molal heat of vaporization of the solvent

(ΔH_0), can be derived from the Clapeyron equation. Thus from the approximate form of that equation is obtained at once the following relation:

$$\frac{dT_0}{dp_0/p_0} = \frac{RT_0^2}{\Delta H_0}.$$

Representing the boiling-point constant by a single letter B, and noting that, so long as the mol-fraction of the solute is small, it is substantially equal to the mol-ratio N/N_0, the law of boiling-point raising for dilute solutions may be expressed by the equation:

$$T - T_0 = B \frac{N}{N_0}.$$

It is evident from this equation that the boiling-point constant B is the ratio of the boiling-point raising to the number of mols of solute which are associated with one mol of solvent; or, briefly, it is the boiling-point raising per mol of solute in one mol of solvent. In chemical literature is commonly recorded, not this boiling-point constant, but another constant, called the *molal boiling-point raising,* which is the boiling-point raising per mol of solute in 1000 grams of solvent.

From the value of either of these constants for a given solvent may be calculated by direct proportion the actual raising of the boiling-point caused by a known number of mols of any solute; or, conversely, there may be calculated the number of mols of solute corresponding to any observed raising of the boiling-point. Therefore the law of boiling-point raising, like Raoult's law from which it has been derived, makes it possible to determine the molecular weight of substances in solution.

The values of the constants obtained for some important solvents by the three methods indicated above and illustrated by Prob. 15 are as follows:

	Water H_2O	Ethyl ether $C_4H_{10}O$	Ethyl alcohol C_2H_5OH	Benzene C_6H_6
Boiling-point constant........	28.6	28.5	25.8	34.0
Molal boiling-point raising....	0.515	2.11	1.19	2.65

Prob. 14. a. Calculate the molal boiling-point raising for water from its boiling-point constant. *b.* Formulate the algebraic relation between the two constants.

Prob. 15.—Methods of Determining the Boiling-Point Constant.— Calculate the boiling-point constant for ethyl alcohol from the following data. *a.* The heat of vaporization of one gram is 206 cal. at the boiling-point 78.3°. *b.* Its vapor-pressure has the values given in Prob. 13. *c.* The boiling-point of a solution of 1 g. naphthalene ($C_{10}H_8$) in 50 g. alcohol is 0.185° higher than that of pure alcohol.

Determination of Molecular Weights and Molecular Composition.—

Prob. 16. *a.* When 10.6 g. of a substance are dissolved in 740 g. of ether ($C_4H_{10}O$), its boiling-point is raised 0.284°. What is the molecular weight of the substance? *b.* The substance is a hydrocarbon containing 90.50% carbon. What is its molecular formula?

Prob. 17. A solution of 3.04 g. benzoic acid in 100 g. ethyl alcohol boils 0.288° higher than pure alcohol. A solution of 6.34 g. benzoic acid in 100 g. benzene boils 0.696° higher than pure benzene. Calculate the molecular weight of benzoic acid in each of these solvents, and state what the results show in regard to its molecular formula in each solvent. Its composition by weight is expressed by the formula $C_6H_5CO_2H$.

The molecular weights of substances are ordinarily found to be the same in the dissolved state as in the gaseous state; but hydroxyl compounds (such as the alcohols and organic acids) form in non-oxygenated solvents (such as benzene or chloroform) double or even more highly associated molecules. This indicates that the molecules of hydroxyl compounds are associated also in the state of pure liquids. Oxygenated solvents (such as water, alcohols, acetic acid, ether, and acetone) have the power of breaking down these associated molecules into the simple ones.

27. Partial Vapor-Pressure of Volatile Solutes. Henry's Law. In addition to Raoult's law, which relates to the vapor-pressure of the solvent in a solution containing a small proportion of a solute, there is another fundamental law which relates to the vapor-pressure of the solute in such a solution. This law, known as *Henry's Law,* may be stated as follows. The partial vapor-pressure of any chemical substance present in small proportion in a solution is proportional to its mol-fraction. That is,

$$p = k\,x,$$

where k is a proportionality-constant dependent on the nature of the substance and of the solvent and on the temperature.

Prob. 18. The total vapor-pressure of a solution containing 3% by weight of ethyl alcohol in water is 760 mm. at 97.11°, and the vapor-pressure of pure water at this temperature is 685 mm. Calculate with the help of Raoult's law and of Henry's law the partial pressures at 97.11° of ethyl alcohol and water in a solution containing 2.00 mol-percent of ethyl alcohol.

It is often convenient in the case of dilute solutions to express the composition in terms of concentration, instead of mol-fraction. By the

concentration of a substance is meant in general the quantity of it per
unit-volume either of the solution or of the solvent. Concentration
expressed in equivalents of solute per liter of solution (N/v) is called
normal concentration (c). This form of concentration, familiar in
volumetric analysis, will be used in this book in connection with prop-
erties, like the electrical conductivity of solutions, which are directly
related to the volume of the solution. Concentration expressed in mols
or formula-weights per liter is called *molal* or *formal concentra-
tion** (c). This is referred sometimes to the volume (v) of the solution,
and sometimes to that of the solvent (v_0); but throughout this book it
will always be used to denote the number of mols or formula-weights of
solute per liter of solvent (N/v_0) at the temperature under consid-
eration.

Prob. 19. Calculate at 25° the normal concentration and the formal
concentration (as above defined) of a solution containing 4.675% H_2SO_4.
The density at 25° of this solution is 1.0279, and that of water is 0.9971.

Henry's law may now be stated as follows: Any chemical substance
present in a gaseous phase and in a solution in equilibrium with it has
at any definite temperature a concentration c in the solution which is
proportional to its (partial) pressure p in the gaseous phase. That is,

$$c/p = K,$$

where K is an equilibrium-constant which is determined by the nature
of the chemical substance and of the solvent and by the temperature.
The equilibrium concentration c is the *solubility* of the substance when
its partial pressure in the gas phase is p, and the equilibrium-constant
K may be called the *solubility-constant* of the gaseous substance in the
solvent. Henry's law is therefore a law of the solubility of gases.

This second form of Henry's law is for dilute solutions substan-
tially equivalent to the first form. For, on the one hand, the mol-
fraction $N/(N_0 + N)$, as it approaches zero, becomes equal to the
mol-ratio N/N_0, which is evidently proportional to the molal concen-
tration N/v_0; and, on the other hand, the vapor-pressure of a substance
in a solution is equal to its partial pressure in a gaseous phase that is
in equilibrium with the solution.

*The number of mols of a substance present in a solution is not necessarily
equal to the number of formula-weights of it added; for the molecules of the
substance, owing to dissociation or association, may have in the solution a
composition different from that represented by the formula.

Henry's law in either of its two forms is conformed to more closely as the pressure of the gas and the concentration of the solute approach zero. Like the other laws of perfect solutions, it usually holds true with an accuracy of 2 to 3 percent, even when the pressure is one atmosphere and the concentration 1 molal.

It is to be noted that Henry's law expresses conditions of equilibrium, and that these conditions are often attained between a gaseous and liquid phase only by long-continued intimate contact.

From a molecular standpoint, Henry's law, like Raoult's law, relates to the distribution of some definite kind of molecule between the gas phase and the liquid phase. Hence in applications of it the same chemical substance in the two phases must be considered. Thus, when the chemical substance SO_2 dissolves in water it is largely converted into H_2SO_3 and its ions H^+ and HSO_3^-; and Henry's law therefore requires, not that the total concentration of solute in the solution, but that the concentration of the SO_2 itself, be proportional to the partial pressure of the SO_2 in the vapor. When, however, the only change in the substance is that it partially combines with the solvent forming a *solvate* (a hydrate in the case of water), then the total concentration may be employed; for the fraction solvated is in dilute solution independent of the concentration of the substance, as may be shown by the mass-action law. Thus, though the substance CO_2 on dissolving in water is partly converted into the hydrate H_2CO_3 (which is substantially unionized, except at very small concentrations), yet the solubility of carbon dioxide gas, as found by determining the total quantity dissolved, changes with the pressure in accordance with Henry's law.— Correspondingly, in applying Henry's law the partial pressure of the chemical substance in the gas phase, not the total pressure of the gas, must be considered. Thus the quantity of carbon dioxide dissolved by water in contact with air is not determined by the pressure of the air, but by the partial pressure of CO_2 in the air.

Prob. 20. A mixture of air and ammonia containing 1 mol-percent of NH_3 is passed at 25° and 1 atm. through water. The saturated solution is found by titration to be 0.553 formal in NH_4OH. Calculate the partial vapor-pressure of NH_3 in a 1 formal solution at 25°. The vapor-pressure of water at 25° is 23.8 mm.

Prob. 21. In a gas burette over mercury 60 ccm. of dry carbon dioxide

at 25° and 1 atm. are placed, 40 ccm. of water are introduced, and the gas and water are shaken together at 25° till equilibrium is reached, keeping the pressure on the gas 1 atm. The volume of the (moist) gas is then found to be 28.9 ccm. Calculate the molal solubility of carbon dioxide in water at 25° when its partial pressure is 1 atm., neglecting effects that influence the result less than 0.5%.

Prob. 22. At 20° 100 ccm. water dissolve 3.4 ccm. of oxygen, 1.7 ccm. of nitrogen, and 3.8 ccm. of argon when the pressure of each gas is 1 atm. *a.* Calculate the corresponding solubility of each gas expressed in terms of its molal concentration. *b.* Calculate the mol-fraction of each constituent in the gas-mixture obtained by shaking water with air at 20°, expelling the dissolved gas by boiling and drying it. Tabulate the molal composition of this gas with that of air (given in Art. 15).

Prob. 23.—Application of Henry's Law to the Determination of the State of Substances in Solution.—The partial vapor-pressure of NH_3 in an aqueous solution 0.3 formal in ammonia and 0.1 formal in $AgNO_3$ is at 25° equal to that in a 0.1 formal solution of ammonia in water. State and explain the conclusion that can be drawn as to the formula of the complex salt formed, considering all the silver nitrate to be combined with ammonia, and assuming that the solubility-constant of the NH_3 is not affected by the silver salt in the solution.

The addition to the water of a salt which does not react with the volatile solute commonly decreases the value of the solubility-constant expressing the ratio of the concentration of the solute in the solution to its pressure in the gas-phase. This phenomenon, which is known as the *salting-out effect,* is subject to the following principles: (1) The decrease of the solubility-constant is approximately proportional to the concentration of the added salt, up to concentrations not much exceeding 1-normal. (2) The fractional decrease per equivalent of salt per liter is roughly the same for a definite salt, whatever be the nature of the solute. (3) This fractional decrease varies greatly with the nature of the salt; thus the decrease caused by 0.1 equivalent of salt per liter of solution varies from about zero in the case of barium nitrate to about 4% in the case of potassium and sodium sulphates.

Prob. 24. The solubility (that is, the concentration of the saturated solution) of carbon dioxide at 25° and 1 atm. is 0.0338 molal in pure water and 0.0331 in a normal NaCl solution. The vapor-pressure of ammonia from a 0.5 molal solution of it in water at 25° is 6.65 mm. Predict from the principles of the salting-out effect the ammonia vapor-pressure for a solution 0.5 molal in NH_3 and 0.5 normal in NaCl.

28. Determination of Equilibrium-Conditions by the Perpetual-Motion Principle.

Prob. 25. A volatile substance S is dissolved in each of two non-miscible solvents, in each of which it has the same molecular weight as in the gaseous state. The two solutions A and B are shaken together at some definite temperature till equilibrium is reached, and are placed, as in Figure 2, in contact with the vapor-phase containing the substance S at a pressure equal to its partial vapor-pressure in solution A. Prove that this pressure must also be the partial vapor-pressure of S in the solution B, by showing that, if it were greater or less, the substance S would pass continuously through the three phases of the system, thus producing perpetual motion, which is impossible.

FIGURE 2

Perpetual motion (of the kind involved in Prob. 25) signifies an ideal process by which an unlimited amount of work might be produced by a system (*i. e.,* an arrangement of matter) operating in surroundings of constant temperature and drawing from them no work. Thus, in the case considered in Prob. 25, if the vapor-pressures of the substance in the two solutions were different, a current of its vapor would flow continuously from one surface to the other, and work could be obtained from the moving vapor for an unlimited period of time, for example, by placing a windmill in the vapor-space. Even though a quantity of heat equivalent to the work produced were taken up from the surroundings, the process would still be a kind of perpetual motion which is impossible, as will be seen later in the discussion of the second law of energetics.

The principle that perpetual motion of this kind is impossible is often employed, as in this instance, for determining the conditions of equilibrium between the different phases of a system. It leads in such cases to the general conclusion that, if two phases are each in equilibrium with a third phase, they must be in equilibrium with each other. It will hereafter be called simply the *perpetual-motion principle.*

29. Law of the Distribution of a Solute between Two Non-Miscible Solvents.— At any definite temperature the ratio between the equilibrium concentrations of a chemical substance S dissolved in
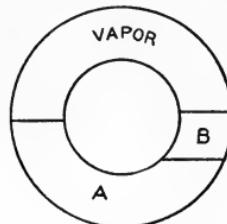
two non-miscible solvents (A and B) is constant, whatever be the values of those concentrations. That is,

$$c_A/c_B = K,$$

where K is a constant, called the *distribution-ratio,* determined by the nature of the substances A, B, and S, and by the temperature.

This law may be generalized so as to be applicable to the distribution of a definite chemical substance between any two kinds of phases. Thus in its general form it includes Henry's law, since the pressure of a gas at any definite temperature is proportional to its concentration (that is, since $p = (N/v) R T = c R T$). It is called the law of distribution between phases, or simply the *distribution-law.*

This distribution law, like Raoult's law and Henry's law, is a limiting law which becomes more exact as the concentrations approach zero.

The distribution-ratio of a solute between water and another solvent is decreased by the addition of a salt to the water in accordance with the principles of the salting-out effect stated in Art. 27.

Prob. 26. Derive the law of the distribution of a volatile solute between two solvents from Henry's law and the conclusion reached in Prob. 25.

Prob. 27. At 25° the vapor-pressure of ammonia above a 0.1 molal solution of it in chloroform is 33.25 mm., and above a 0.5 molal solution of it in water is 6.65 mm. *a.* What is the distribution-ratio of ammonia between water and chloroform? *b.* What would be its distribution-ratio between a 0.5 normal NaCl solution and chloroform?

Prob. 28. The distribution-ratio of an organic acid between water and ether at 20° is 0.4. A solution of 5 g. of the acid in 100 ccm. water is shaken successively with three 20-ccm. portions of ether. *a.* How much acid is left in the water? *b.* How much acid would have been left in the water if the solution had been shaken once with a 60-ccm. portion of ether?

Prob. 29. An aqueous solution 0.25 formal in KCl and 0.20 formal in $HgCl_2$ is shaken with an equal volume of benzene at 25°. The benzene phase is found by analysis to contain 0.0057 mol $HgCl_2$ per liter, but no KCl. The distribution-ratio of $HgCl_2$ between water and benzene at 25° is 13.3. *a.* Calculate the total concentration of mercuric chloride in the aqueous phase and the concentration of the part of it which is combined with the potassium chloride (neglecting the salting-out effect). *b.* The complex salt has been shown by other measurements to be $KHgCl_3$. Tabulate its concentration and those of the (uncombined) KCl and $HgCl_2$.

VAPOR–PRESSURE AND BOILING–POINT OF CONCENTRATED SOLUTIONS

30. Relation between the Vapor-Pressure and Molal Composition of Perfect Concentrated Solutions.—Concentrated solutions may be divided for purposes of consideration into two groups as follows. One group consists of those solutions whose formation out of their pure components (when these are liquid) is not attended by any considerable change of temperature or volume, and whose properties in general are approximately the sum or average of those of the pure components. The characteristic of such solutions is that neither component exerts a specific influence on the properties of the other component. Such solutions conform approximately—more closely as the condition characterizing them is more nearly fulfilled—to the laws of perfect solutions. The other group consists of those solutions whose components exert a marked influence upon one another. For these solutions no general laws are known.

In the case of solutions belonging to the first of these groups the vapor-pressure of each component conforms approximately to Raoult's law. In other words, the partial vapor-pressure of each component is approximately equal to the product of its mol-fraction in the solution by its vapor-pressure in the pure state, whatever be the proportion in which the components are present; that is, $p_A = p_{0A}x_A, \ p_B = p_{0B}x_B, \ldots$

The method commonly employed for determining the partial vapor-pressures of the components of solutions at any definite temperature is to distil off a small fraction from a large volume of the solution, adjusting the pressure on the liquid so that it boils at this temperature. The composition of the distillate is then determined by chemical analysis or by the measurement of some physical property, such as density; and from this composition and the pressure under which the distillation took place the partial vapor-pressures are calculated, as illustrated in the following problem.

Prob. 30. A solution of two substances A and B containing N_A mols of A and N_B mols of B boils at the temperature T when a pressure of p is exerted upon it. The first portion of distillate consists of N_A' mols of A and N_B' mols of B. Derive an algebraic expression for the partial vapor-pressures p_A and p_B of the two substances in the solution, explaining the principles involved.

Prob. 31. At 50° the partial vapor-pressures of benzene and of ethylene chloride in solutions of these two substances have been found experimentally to have the following values:

Mol-fraction of C_6H_6	Vapor-pressure of C_6H_6	Vapor-pressure of $C_2H_4Cl_2$
1.000	268.0 mm.	0.0 mm.
0.707	190.0	69.0
0.478	128.0	124.0
0.246	66.0	178.0
0.000	0.0	236.0

a. Plot on a large scale these partial vapor-pressures, and the corresponding total vapor-pressures, as ordinates against the mol-fractions as abscissas. Show that the three graphs are in almost complete accord with Raoult's law. *b.* Calculate the mol-fraction of benzene in the vapor which at 50° is in equilibrium with each of the three solutions for which the data are given in the above table. *c.* On a new larger-scale vapor-pressure composition diagram (with ordinates covering only the interval of 230–270 mm.) draw a line showing the variation of the total vapor-pressure with the mol-fraction of the liquid mixture. Plot also on this diagram the compositions of the vapor calculated in *b* against the total vapor-pressures, considering that the abscissas now represent the mol-fraction of benzene in the vapor.

*Prob. 32.—Distillation at Constant Temperature.—*At 50° a small fraction is distilled off from a large volume of a solution containing equimolal quantities of benzene and ethylene chloride, and this distillate is redistilled at 50°. Derive from the diagram of Prob. 31 the mol-fraction of benzene in the first part of the second distillate.

31. Relation between the Boiling-Point and Molal Composition of Perfect Concentrated Solutions.—When a solution of any concentration contains only one volatile component and the vapor-pressure of this component conforms to Raoult's law, an exact differential expression for the rise in boiling-point dT of the solution produced by an increase dx in the mol-fraction of the solute can be obtained by combining the appropriate equations (as in Prob. 33). This expression is:

$$dT = \frac{R\,T^2}{\Delta H_0}\,\frac{dx}{1-x}.$$

In this expression ΔH_0 represents the molal heat of vaporization of the pure solvent at the temperature T. The expression can be integrated (as in Prob. 34), usually without significant error, under the assumption that ΔH_0 does not vary within the temperature-interval involved.

The boiling-point can also be determined graphically from the vapor-pressure curve of the solvent as given by direct measurements and from that of the solution as computed by Raoult's law, as was illustrated in Prob. 13.

When a solution contains two volatile components whose partial vapor-pressures both conform to Raoult's law, its boiling-point can best be derived graphically from the vapor-pressures of the pure substances (as in Prob. 35).

Prob. 33.—Boiling-Point of Perfect Concentrated Solutions with One Volatile Component.—A consideration (like that in Prob. 13) of the vapor-pressure curves shows that the following relation holds true for any solution with one volatile component, whatever be its concentration:

$$\left(\frac{\partial T}{\partial x}\right)_p = - \left(\frac{\partial T}{\partial p}\right)_x \left(\frac{\partial p}{\partial x}\right)_T.$$

a. State in words what each of these partial derivatives signifies. *b.* Find from the approximate Clapeyron equation (Art. 22) and from the Raoult equation, respectively, expressions for the last two of these partial derivatives. *c.* Obtain by substituting these expressions in the above given equation and transforming the differential equation given in the preceding text. (The symbol ΔH, which in the Clapeyron equation as applied in this derivation represents the quantity of heat taken up from the surroundings when 1 mol of solvent vaporizes out of an infinite quantity of the solution at the temperature T, can be shown to be identical, in case the solution conforms to Raoult's law, with the molal heat of vaporization of the pure solvent at the temperature T. It can also be shown, by deriving the partial derivatives from the exact Clapeyron equation and from the more exact Raoult equation (given at the end of Art. 24), that the boiling-point equation given in the preceding text holds true with substantial accuracy up to a mol-fraction of solute of 5% to 10%, even when the vapor deviates from the perfect-gas law.)

Prob. 34. Integrate the equation given in the text, assuming that the heat of vaporization does not vary with the temperature, so as to obtain a relation between the boiling-point of the solution, the boiling-point of the pure volatile component, and its mol-fraction in the solution. *b.* Calculate the boiling-point of a solution consisting of 10 mols of a non-volatile solute and 90 mols of benzene. The heat of vaporization of one gram of benzene at its boiling-point 80.3° is 93.0 cal.

Prob. 35.—Boiling-Point of Perfect Solutions with Two Volatile Components.—The vapor pressure at.. 80°, 83°, 86°, 89°, 92° of a pure liquid A is................. 560, 610, 665, 725, 790 mm., and of a pure liquid B is............ 400, 435, 475, 520, 570 mm.

*This problem may be omitted in briefer courses or by those unfamiliar with partial derivatives.

a. With the aid of these data and Raoult's law, draw on a large-scale vapor-pressure–composition diagram for each temperature two lines—one representing the total vapor-pressure of any solution of A and B; and the other representing the partial vapor-pressure of A above any solution. *b.* Determine from the plot the composition of the liquid which at 570 mm. boils at each of these temperatures; also the composition of the vapor which is in equilibrium with each of these solutions at its boiling-point. Determine also the boiling-point of the pure liquid A at 570 mm., and tabulate all of these results. *c.* On another large-scale diagram plot against these liquid-compositions the boiling-points as ordinates. Plot also the vapor-compositions against the corresponding boiling-points.

Distillation at Constant Pressure of Perfect Solutions with Two Volatile Components.—

Prob. 36. A solution of 100 mols of each of the liquids A and B of Prob. 35 is distilled at 570 mm. until its boiling-point rises 0.5°. *a.* Find from the diagram of Prob. 35*c* the molal compositions of the first and last portions of the distillate. *b.* Regarding the composition of the whole distillate as the mean of that of its first and last portions (which is approximately true when only a small fraction of the liquid distils over), calculate the number of mols of A and of B in the distillate and in the residue. *c.* The distillation of the residue is continued till its boiling-point rises 0.5° more. Calculate as in *b* the number of mols of A and B in this second distillate and in the residue. *d.* Tabulate the number of mols of A and of B in the original liquid, the first distillate, the second distillate, and the final residue; the mol-fraction of A in each of these liquids; and the boiling-point of each of them.

Prob. 37. *a.* The first distillate obtained in Prob. 36*a* is redistilled until the residue attains the composition of the second distillate obtained in Prob. 36*c.* Find the mol-fraction of A in the new distillate and its boiling-point. *b.* The residue is now mixed with the second distillate obtained in Prob. 36*c,* and the distillation is continued till the residue has the composition of the residue obtained in Prob. 36*c.* Find the mol-fraction of A in the distillate thus obtained and its boiling-point. *c.* Tabulate the composition and the boiling-point of the original equimolal solution and of the three fractions into which it has now been resolved.

Note.—It is clear from the diagram of Prob. 35*c* that any perfect solution submitted to distillation resolves itself into a distillate containing a larger proportion, and into a residue containing a smaller proportion, of the more volatile component. It is evident that, in consequence of this behavior, the two components can be completely separated from each other by repeated fractional distillation, carried out as illustrated by Probs. 36 and 37.

32. Relation between the Vapor-Pressure and Composition of Concentrated Solutions in General.— There are comparatively few actual solutions which fulfil strictly the criterion stated in Art. 30 of being formed out of their components without any change of temperature or volume; and correspondingly, comparatively few concentrated solutions conform completely to Raoult's law of perfect solutions. The law is therefore to be regarded as a limiting law, from which actual solutions deviate to an extent which is as a rule roughly indicated by the magnitude of the changes of temperature and volume attending the mixing of the components.

The data given below illustrate the magnitude of the deviations from the law for a variety of solutions. The first two columns of figures show the change of temperature and the percentage change of volume which result when equimolal quantities of the two substances at the same temperature are mixed. The last column shows the percentage difference between the observed and calculated values of the total vapor-pressure of the equimolal solution. This deviation of the total pressure corresponds roughly to the deviations of the partial pressure from Raoult's law for the reason that the partial pressures of the two components deviate from the law in the same direction.

No.	Components	Change of Temperature	Change of Volume	Deviation of Pressure
1.	CH_3OH and C_2H_5OH	— 0.10°	0.00%	+ 0.1%
2.	C_6H_6 and $C_6H_5CH_3$	— 0.45	+0.16	— 0.4
3.	$C_2H_5C_2H_3O_2$ and $C_2H_5C_3H_5O_2$	— 0.02	+0.02	+ 0.6
4.	C_6H_6 and $C_2H_4Cl_2$	— 0.35	+0.34	+ 0.1
5.	C_6H_6 and C_6H_{14}	— 4.7	+0.52	+11.
6.	$(CH_3)_2CO$ and $CHCl_3$	+12.4	—0.23	—20.
7.	C_6H_6 and C_2H_5OH	— 4.2	0.00	+50.
8.	H_2O and C_2H_5OH	+ 3.0	—2.56	+30.

It will be seen from the table that there is a parallelism between the changes of temperature or volume and the deviations from Raoult's law. Thus with the first four pairs of substances, where these changes are small, the deviations are less than 1%; and with the last four pairs, where either the temperature or volume change is large, the deviations are so great that Raoult's law cannot be said to afford even a rough estimate of the actual values of the pressure.

There have not been discovered any very definite relations between the magnitude of the deviations and the nature of the substances; but the following rules furnish useful indications: (1) Substances which are closely related chemically, such as the neighboring members of the same homologous series (like the first three pairs of substances in the table), or those which differ only in that they contain a different halogen (like chlorbenzene and brombenzene). conform very closely to Raoult's law, whether or not the molecules of the pure substances are associated in the way described in the last paragraph of Art. 26. (2) Substances not closely related chemically which have non-associated molecules sometimes conform very closely to Raoult's law (like the fourth pair in the table), and sometimes show large deviations from it (like the fifth and sixth pairs). In most cases where the observed pressure is less than the calculated pressure, these deviations are probably due to the formation of a compound between the two substances (as has been shown to be true of the sixth pair in the table). In those cases (like that of the fifth pair) where the observed pressure is greater than the calculated pressure, the excess of pressure is probably due to a physical effect arising from a change in the attractions between the molecules. (3) When a substance with associated molecules is mixed with one with unassociated molecules, the vapor-pressure of the solution is much greater than that calculated by Raoult's law, as is illustrated by the data for ethyl alcohol and benzene, the seventh pair in the table. This effect is doubtless due in part to the breaking down of the associated molecules of the one substance by the dilution with the other substance, whereby the partial pressure of the first substance is increased. (4) Substances which are only partially miscible (like ether and water) form solutions whose vapor-pressures are much larger than those required by Raoult's law.

In connection with these deviations it should be borne in mind that, as the mol-fraction of any component approaches unity (so that the solution becomes dilute with respect to the other component). its partial vapor-pressure always approaches that required by Raoult's law, and the partial vapor-pressure of the other component conforms to Henry's law, however great the deviation may be when both components are present in large proportion.

Prob. 38. Explain by reference to Raoult's law: *a*, why the formation of a non-volatile compound AB between the two components A and B of a solution causes the vapor-pressure of the solution to be less than that required by Raoult's law; *b*, why a substance which in the pure state has associated molecules may have an abnormally large partial vapor-pressure in a solution.

Prob. 39. *a.* Draw on a large-scale diagram vapor-pressure curves representing the partial vapor-pressure at 35.2° of carbon bisulphide and of acetone in solutions of these components throughout the whole range of composition. In accordance with the principle that all dilute solutions conform approximately to Raoult's law and Henry's law, assume these laws to hold with this pair of components up to 5 mol-percent; and make use of the following values in millimeters of the vapor-pressures at 35.2°:

Mol-percent of CS_2	0	1	20	40	60	80	99	100
Vapor-pressure of CS_2	0	17.8	274	377	425	460	—	518
Vapor-pressure of acetone	353	—	289	255	228	187	20.1	0

b. On the same diagram draw a curve representing the total vapor-pressures of the solutions. Draw on the diagram dotted lines showing what the partial and total vapor-pressures would be if the solutions behaved as perfect solutions. *c.* Calculate the mol-percents of CS_2 in the vapor in equilibrium with the 5, 20, 40, 60, 80, and 95 mol-percent liquid solutions; and on the same diagram plot these vapor-compositions against the total vapor-pressures and draw a dotted line through the points.

Note.—With the aid of this plot the behavior of any solution of carbon bisulphide and acetone when submitted to distillation at 35.2° could evidently be predicted.

33. Relation between the Boiling-Point and Composition of Concentrated Solutions in General.—The boiling-point–composition curves for solutions whose vapor-pressures do not conform to Raoult's law can be based only upon direct experimental determinations of the boiling-points of solutions of known composition and upon analyses of the corresponding distillates. All that can be done, in the way of generalization, is to consider the different types of curves to which different pairs of substances conform. Figure 3 shows the three types of curves exhibited by substances miscible in all proportions. In each case the solid curve shows the compositions (expressed as mol-fractions) and corresponding boiling-points of the liquid solutions at one atmosphere; and the broken curve shows the composition of the vapor that is in equilibrium with these solutions. Thus any point on a broken curve represents the composition of the vapor of the liquid solution whose point lies in the same horizontal line.

Curve I is the experimentally determined curve for solutions of carbon tetrachloride (b. pt., 76.7°) and carbon bisulphide (b. pt., 46.3°). Curve II is that for solutions of acetone (b. pt., 56.2°) and chloroform (b. pt., 61.3°). Curve III is that for solutions of acetone (b. pt., 56.2°) and carbon bisulphide (b. pt., 46.3°).

Solutions of type I, when subjected to fractional distillation, behave like perfect solutions (which form a special case of this type), and may like them be finally resolved into the pure components. The behavior of solutions of types II and III on fractional distillation is shown in the following problems.
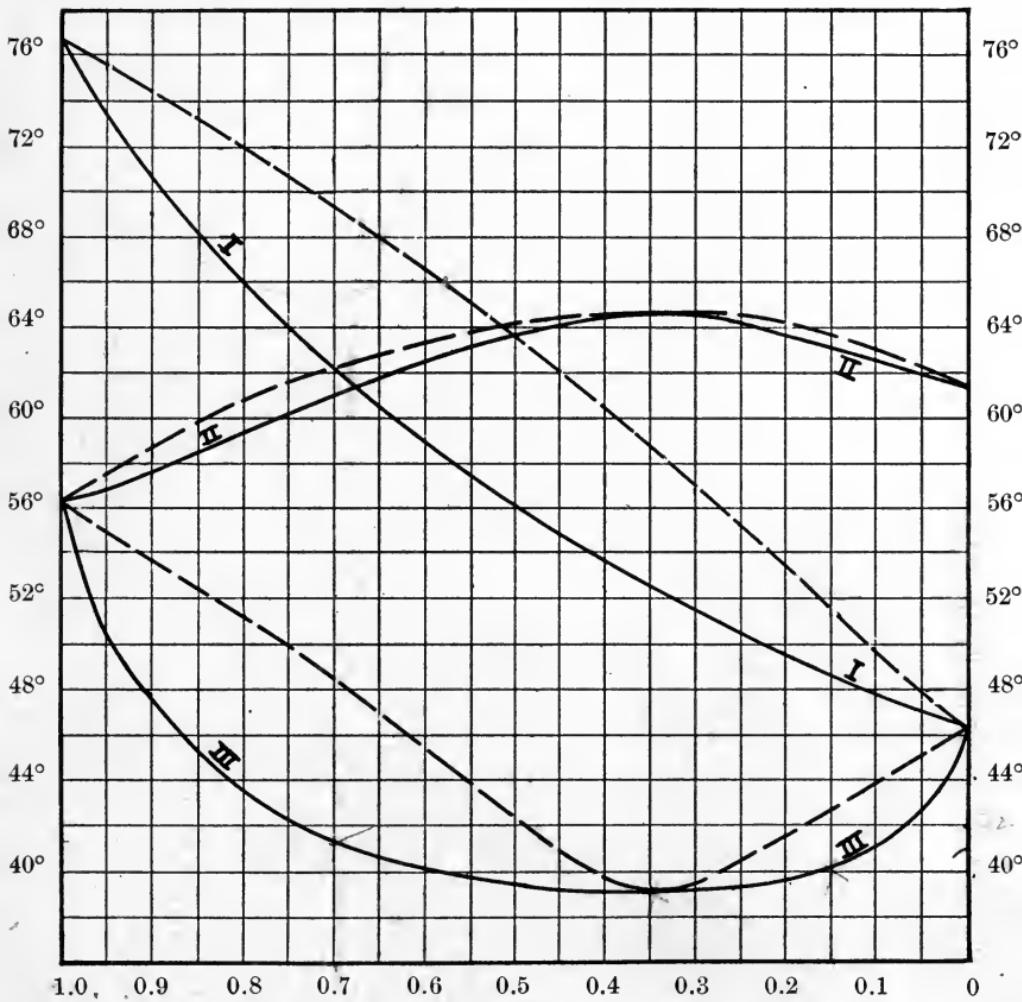
FIGURE 3

Prob. 40. a. Determine from curve III in Figure 3 the boiling-point and composition of the first portion of distillate obtained by partial distillation of solutions of acetone and carbon bisulphide containing 70 mol-percent of acetone, 15 mol-percent of acetone, and 35 mol-percent of acetone, respectively. Tabulate the boiling-point and composition of each solution and distillate. *b.* State in what respects each distillate and each residue differ from the solution from which it was obtained. *c.* If each of the solutions were submitted repeatedly to fractional distillation, what would be the composition of the products finally obtained as distillate and as residue? *d.* If of the 70 mol-percent solution 1000 g. were so fractionated, what weight of each product would be obtained?

Prob. 41. By reference to curve II in Figure 3 answer the same questions for solutions of acetone and chloroform as are asked in Prob. 55, *a, b,* and *c,* for solutions of acetone and carbon bisulphide.

Just as the solid lines in such temperature-composition diagrams show the boiling-points of any liquid solution, so the broken lines show the condensation-point at one atmosphere of vapor of any composition; the composition of the liquid which first condenses out of it being given by the corresponding point on the solid line. Such diagrams therefore serve to predict the behavior of vapors when subjected to fractional condensation, as illustrated by the following problem.

Prob. 42. a. A vapor composed of equimolal quantities of carbon tetrachloride and carbon bisulphide is cooled at 1 atm. till condensation begins. By referring to curve I in Figure 3 find the temperature at which condensation begins, and the composition of the condensate. *b.* The vapor is gradually cooled, removing the condensate as it forms, till the temperature falls to 60°. Find the composition of the condensate which is now separating, and that of the residual vapor. *c.* Tabulate the composition (50 mol-percent) of the original vapor, the average composition of the condensate obtained from it in *b,* and the composition of the residual vapor. Include in the table also the composition of the liquid which upon distillation would furnish the original vapor.

The processes used in chemical practice for the separation of volatile liquids, such as alcohol and water, involve fractional distillations and condensations taking place in accordance with the principles here considered.

34. Freezing-Point and Its Relation to Vapor-Pressure.—The freezing-point of a liquid is that temperature at which the solid solvent and the liquid coexist in equilibrium with each other. The solid which separates from the solution commonly consists of the pure solvent; and this is assumed to be the case throughout the following considerations. In any such case the freezing-point of a solvent is lowered by dissolving another substance in it.

Prob. 43. Prove that at the freezing-point of a solution its vapor-pressure and that of the solid which separates from it must be equal, by showing that otherwise perpetual motion would result.

Prob. 44. The vapor-pressures of ice and (supercooled) water between 0° and —4° are as follows:

	0°	—1°	—2°	—3°	—4°
Water...........	4.58	4.26	3.96	3.68	3.41 mm.
Ice.............	4.58	4.22	3.89	3.59	3.30 mm.

a. Calculate by Raoult's law the vapor-pressure at each of these temperatures of a solution consisting of 3 mols of solute and 97 mols of solvent. Plot on a diagram the vapor-pressures of this solution, of water, and of ice as ordinates against the temperatures as abscissas, using a scale large enough to enable 0.001 mm. to be estimated (by including on it pressures ranging only from 3.30 to 4.60 mm.). *b.* Determine from the plot the freezing-point of the solution.

With the aid of a diagram like that of the preceding problem, but including also the vapor-pressure curves of a second solution, it can be shown from the geometrical relations that for dilute solutions the lowering of the freezing-point is proportional to the lowering of the vapor-pressure of the solvent at its freezing-point. It can also be shown that the proportionality-constant is dependent on the difference in the slopes of the vapor-pressure curves for the solid solvent and for the liquid solvent.

35. Relation between Freezing-Point-Lowering and Molal Composition.—From Raoult's law of vapor-pressure lowering and from the Clapeyron equations expressing the change of the vapor-pressure of the solid and the liquid solvent with the temperature, the following equation can be derived by a method similar to that used in Arts. 25

and 26 for obtaining the corresponding expression for the boiling-point raising:

$$T_0 - T = B\,\frac{N}{N_0} = \frac{R\,T_0^2}{\Delta H_0}\,\frac{N}{N_0}.$$

In this equation T_0 is the freezing-point of the solvent, T that of a solution of N mols solute in N_0 mols solvent, B a quantity characteristic of the solvent called its *freezing-point constant,* and ΔH_0 the heat absorbed by the fusion of one mol of the solvent at T_0.

In place of this freezing-point constant, the *molal freezing-point lowering,* defined analogously to the molal boiling-point raising, is commonly recorded in chemical literature.

Prob. 45. When one gram of ice at 0° melts, the heat absorbed is 79.7 cal. *a.* What is the freezing-point constant for water? *b.* What is its molal freezing-point lowering?

Prob. 46. A solution of 0.60 g. acetic acid in 50.0 g. water freezes at —0.376°. A solution of 2.32 g. acetic acid in 100 g. benzene freezes 0.970° lower than pure benzene. The freezing-point constant for benzene is 65.4. Calculate the molecular weight of acetic acid in each of these solvents, and state what the results show in regard to its molecular formula in each solvent.

The following differential expression for the freezing-point of perfect solutions of any concentration may be obtained by formulating the appropriate equations:

$$-d\,T = \frac{R\,T^2}{\Delta H_0}\,\frac{d\,x}{(1 - x)}.$$

In this equation $-d\,T$ denotes the lowering produced in the freezing-point T of a solution by increasing the mol-fraction x of the solute by dx, and ΔH_0 denotes the heat absorbed by the fusion of one mol of the solid solvent at T. This equation is exact at any concentration up to which Raoult's law holds true. It may be integrated, commonly without significant error, under the assumption that ΔH_0 does not vary within the temperature-interval involved.

The freezing-point of other concentrated solutions, for which there is no general law, cannot be calculated from the molal composition. The relation between freezing-point and molal composition can, of course, be experimentally determined; and the results may be clearly represented by freezing-point–composition diagrams, analogous to the boiling-point–composition diagrams. Such diagrams are considered in Chapter VII.

OSMOTIC PRESSURE OF SOLUTIONS

36. Osmotic Pressure.—When a solution S is separated from a pure solvent W, as illustrated in Figure 4, by a wall aa which allows this solvent to pass through it, but prevents entirely the passage of the solute, the solvent is drawn through the wall into the solution. This flow of solvent may, however, be prevented by exerting a pressure p_2 on the solution greater by a definite amount than the pressure p_1 upon the pure solvent; and the solvent may be forced out of the solution by exerting a still greater pressure upon the solution. The difference of pressures on solution and solvent which produces a condition of equilib-

FIGURE 4

rium such that there is no tendency of the solvent to flow in either direction is called the *osmotic pressure P* of the solution.
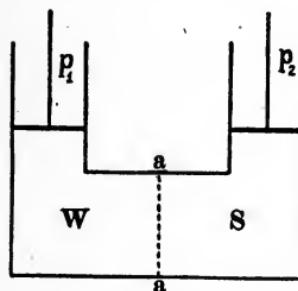
Walls of the kind just described are known as *semipermeable walls*. Certain animal membranes, such as parchment or bladder, are permeable for water, but not for certain solutes of high molecular weight (the so-called colloids). The walls of some animal and plant cells are very perfect semipermeable walls. The most satisfactory artificial semipermeable walls have been made by precipitating copper ferrocyanide within the pores of an unglazed porcelain cell, which gives the precipitate sufficient rigidity to withstand high osmotic pressures. The cell, filled with the solution and immersed in pure water, is connected with a manometer whose mercury column is in direct contact with the solution. By means of such cells exact measurements of the osmotic pressure of aqueous solutions of cane-sugar and glucose have been made up to pressures of 25 atmospheres.

Osmotic pressure plays a very important part in the physiological processes taking place in the bodies of animals and plants. In the study of the general principles of chemistry, it is of value because it is a property which, like vapor-pressure, enables the various properties of solutions to be correlated and their energy relations to be treated upon the basis of one simple fundamental concept. The correspondence shown in Art. 38 to exist between the laws of the osmotic pressure of dilute solutions and those of the pressure of perfect gases makes possible, moreover, a closely analogous treatment of these two states.

37. Relation of Osmotic Pressure to Vapor-Pressure.— In the osmotic arrangement represented in Figure 4, when the pressures P_1 and P_2 are such that there is equilibrium and therefore no tendency for the solvent to pass through the semipermeable wall, it follows from the perpetual motion principle that the vapor-pressure of the solvent in the pure state must be equal to its vapor-pressure in the solution. For, if a vapor phase were in contact (through walls permeable only for the vapor) both with the solvent and the solution, there would evidently be a continuous flow of the solvent-substance through the vapor-phase and back through the wall between the two liquid phases, unless its vapor-pressures in these liquid phases were equal. That this condition is realized results from the fact that the vapor-pressure of a liquid is increased by increasing the pressure upon it. Thus the larger pressure P_2 on the solution increases its vapor-pressure up to the value of the vapor-pressure of the solvent under the smaller pressure P_1. From a quantitative consideration of the effect of pressure on vapor-pressure a relation between the vapor-pressure and osmotic pressure of solutions can be derived, as shown in the following problems.

Effect of Pressure on the Vapor-Pressure of Liquids.—

*Prob. 47. Consider a column of a pure solvent contained in a porous tube impermeable to the liquid solvent, but permeable to its vapor; and consider this tube to be surrounded by the vapor of the solvent; the whole system being at a constant temperature T. When there is equilibrium the vapor-pressure of the solvent at any level must evidently be equal to the pressure of the vapor at that level. The pressure of the liquid or of the vapor must, however, be greater at a lower than a higher level by the (hydrostatic) pressure of the intervening column of liquid or vapor. *a.* Formulate an expression for the increase dP of the pressure P of the liquid, and one for the increase dp of the pressure p of the vapor, corresponding to a decrease $(-dh)$ in the height h. *b.* By combining these expressions and making appropriate substitutions, derive the fundamental equation $dp/dP = v_0/v$, in which v_0 is the volume of any definite weight of the liquid at the pressure P and temperature T, and v is the volume of the same weight of the vapor at the pressure p and temperature T. *c.* Integrate this equation between the limits p_1, P_1, and p_2, P_2, assuming that the vapor conforms to the perfect-gas laws and that the volume of the liquid does not vary with the pressure upon it.

*Prob. 48. Find the ratio of the vapor-pressure of water at 4° and 10 atm. to that at 4° and the pressure of the saturated vapor.

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*Problems with asterisks attached are not essential to the subsequent considerations and may be omitted in brief courses on the subject.

Relation of Osmotic-Pressure to Vapor-Pressure.—

*Prob. 49. *a.* How much must the pressure on water be reduced in order that it may be in equilibrium through a semipermeable wall with an aqueous solution which has at 25° a vapor-pressure 98% as great as that of water? (The water must evidently be subjected to a negative pressure or suction. With proper precautions liquids have been subjected to negative pressures of several atmospheres, without the column breaking.) *b.* What is the osmotic pressure of this solution?

The preceding problems show that the osmotic pressure P at the temperature T of any solution consisting of N mols of solute and N_0 mols of solvent (whose volume in the pure state is v_0) is given by the expression:

$$P = \frac{N_0\,R\,T}{v_0}\ \log\frac{p_0}{p}.$$

In this expression p_0 represents the vapor-pressure of pure solvent and p that of the solvent in the solution. The expression is substantially exact even at large concentrations, provided the vapor conforms to the perfect-gas laws.

Prob. 50. At 100° the vapor-pressure of a solution consisting of 28 g. NaCl and 100 g. H_2O is 624 mm. What is its osmotic pressure? The specific volume of water at 100° is 1.043.

38. Relation between Osmotic Pressure and Molal Composition.— For a solution whose vapor-pressure conforms to Raoult's law, the equation derived in Art. 37 can be transformed into the following one:

$$P\,v_0 = N_0\,R\,T\ \log\left(1 + \frac{N}{N_0}\right).$$

For dilute solutions, for which N/N_0 is small, this equation can be simplified by expanding the logarithmic term into a series, as shown in Prob. 51, to the following expression:

$$P\,v_0 = N\,R\,T,\text{ or } P = c\,R\,T.$$

In these expressions P is the osmotic pressure at the temperature T of a solution consisting of N mols of solute and N_0 mols of solvent whose volume in the pure state is v_0, c is the molal concentration, and R is the gas-constant.

The osmotic pressure of concentrated solutions to which Raoult's law does not apply cannot be calculated from the composition of the solution. It may, however, be determined not only by direct measurement, but also from vapor-pressure measurements, as shown in Art. 37.

Prob. 51. Derive the two equations given in the preceding text.

Prob. 52. The lower end of a vertical tube is closed with a semipermeable wall and is dipped just beneath the surface of a pure solvent. A 0.1 mólal solution of cane-sugar ($C_{12}H_{22}O_{11}$) of density 1.014 is poured into the tube until the hydrostatic pressure at the semipermeable wall is sufficient to prevent water from entering the solution. The temperature is 4°. What is the height of the column in meters?

REVIEW OF THE MOLAL PROPERTIES OF SOLUTIONS

39. Review Problems.

Prob. 53. *a.* Summarize the equations expressing for dilute solutions the approximate relations between molal composition and (1) vapor-pressure, (2) boiling-point, (3) freezing-point, (4) osmotic pressure. State explicitly what each symbol signifies.

Prob. 54. Summarize the corresponding equations which hold true for perfect solutions of any concentration.

Prob. 55. *a.* Calculate by the laws of dilute solutions, using the data given below, the fractional vapor-pressure-lowering, the boiling-point-raising, the freezing-point-lowering, and the osmotic pressure at 5.5° of a solution A containing 0.1 mol of a nonvolatile solute S in 1000 g. benzene. *b.* Calculate by the laws of perfect concentrated solutions the values of the same quantities for a solution B containing 2 mols of the solute S in 1000 g. benzene. Calculate the ratio of each of these values to the corresponding one for solution A. (Note that the value of this ratio would be 20.0, if the equations for dilute solutions were applicable to solution B.) *c.* If the solute in solution B were volatile and at the boiling-point of the solution had a partial pressure of 20 mm., what would be the boiling-point of the solution? Data: The heat of fusion of one gram of benzene at its freezing-point, 5.5°, is 30.2 cal. The heat of vaporization of one gram of benzene at its boiling-point, 80°, is 93.0 cal. The density at the freezing-point is 0.895.

Prob. 56. *a.* Carbon bisulphide boils at 46° at 1 atm. Its molal heat of vaporization at this temperature is 6430 cal. What is its boiling-point constant? *b.* A solution of 15.5 g. phosphorus (at. wt., 31.0) in 1000 g. CS_2 boils 0.300° higher than pure carbon bisulphide. What is the molecular weight and what is the molecular formula of phosphorus in this solvent?

Prob. 57. If 127 g. iodine (at. wt., 127) were added to the solution of Prob. 56*b*, how much higher than the boiling-point of pure carbon bisulphide would that of the solution be: *a*, in case the iodine remained uncombined in the form of I_2; *b*, in case it all combined with the phosphorus forming P_4I_8; *c*, forming P_2I_4; *d*, forming PI_2?

Prob. 58. Human blood freezes at —0.56°. What is its osmotic pressure at 37°?

Prob. 59. At 25° the distribution-ratio of Br_2 between carbon tetrachloride and water is 38; and the pressure of bromine above a 0.05 molal solution of Br_2 in water is 50 mm. If one liter of this solution be shaken with 50 ccm. carbon tetrachloride, what will be the pressure of the bromine over the carbon-tetrachloride phase? (Bromine exists in all three phases only as Br_2.)

Prob. 60. When ethyl acetate and water are shaken together at 20°, two liquid phases result, one phase containing 1.75 mol-percent. and the other 86.8 mol-percent ethyl acetate. *a.* Show that, even though Raoult's law may hold for one component in one phase, it cannot hold for the same component in the other phase. *b.* Calculate the partial vapor-pressures of ethyl acetate and water over the mixture, assuming, since the solutions are moderately dilute, that Raoult's law applies to the solvent in each phase. At 20° the vapor-pressure of pure ethyl acetate is 73 mm., and that of water is 17.4 mm. *c.* Calculate the partial vapor-pressures of the two components in a solution containing 1.00 mol-percent of ethyl acetate.

Prob. 61. Aniline ($C_6H_5NH_2$) is distilled with steam at 1 atm. The vapor-pressure of aniline is 46 mm. at 100° and 40 mm. at 97°. Water and aniline have limited solubilities in each other; one phase containing at 100° 1.5 mol-percent of aniline, and the other 68 mol-percent of aniline. Find the boiling-point of the mixture, and the number of grams of aniline distilling over with each gram of water. Assume that the solubilities do not change appreciably within the small temperature interval, and that the vapor-pressure of the aniline in the 68 mol-percent solution is lowered only half as much as Raoult's law requires. (This last assumption is a rough estimate based on the considerations that the partial vapor-pressure of the aniline in the 68 mol-percent solution is less than that of pure aniline and that, in accordance with statement (4) on page 34, it is greater than that required by Raoult's law. In the absence of more definite knowledge it is obviously best to assume that the actual vapor-pressure lies midway between these two limiting values.)

Prob. 62. At 1 atm. pure nitric acid has a boiling-point of 86°. A solution of nitric acid and water of the composition $HNO_3 + 1.6 H_2O$ distils at 1 atm. at a constant temperature of 121°. Make a diagram showing the character of the boiling-point–composition curve for this pair of substances. Draw in on the diagram a curve representing in a general way the composition of the vapor in equilibrium with any solution at its boiling-point. State what products would finally result as distillate and residue from the fractionation of the three solutions, $HNO_3 + H_2O$, $HNO_3 + 1.6 H_2O$, $HNO_3 + 3 H_2O$.

Prob. 63. Upon partial distillation at constant pressure a solution of two components A and B containing 20% A, having a boiling-point of

80°, yields a residue containing 15% A; and a mixture containing 75% A, having a boiling-point of 60°, yields a distillate containing 70% A. Draw a diagram which will show in a general way the character of the liquid-composition and of the vapor-composition curve. Predict what products would finally result as distillate and residue from the fractionation of the 20% and of the 75% solution.

CHAPTER IV

PROPERTIES OF SOLUTIONS RELATED TO IONIC COMPOSITION

EFFECT OF IONIZATION ON THE MOLAL PROPERTIES OF SOLUTIONS

40. Abnormal Effects of Salts on the Vapor-Pressure and Related Properties of Water, and their Explanation by the Ionic Theory.—In dilute solution the effect of salts of the uniunivalent type, such as sodium chloride or silver nitrate, on the vapor-pressure of water and on the other related properties is nearly twice as great, and the effect of salts of the unibivalent type, such as potassium sulphate and barium chloride, is nearly three times as great, as it would be if each formula-weight yielded a single mol in the solution. Strong acids and bases show a similar behavior. These and other facts have led to the conclusion that these substances are largely dissociated in aqueous solution. For example, NaCl dissociates into Na^+ and Cl^-; HNO_3 into H^+ and NO_3^-; K_2SO_4 into K^+, K^+, and SO_4^{--}; and $Ba(OH)_2$ into Ba^{++}, OH^-, and OH^-. Tri-ionic substances also dissociate partially into intermediate ions; thus K_2SO_4 into KSO_4^- (and K^+), and $Ba(OH)_2$ into $BaOH^+$ (and OH^-).

The electrical behavior of the solutions indicates that these dissociation-products differ from ordinary substances in that their molecules are electrically charged. These charged substances are called *ions;* and to their formulas $+$ or $-$ signs are attached, as in the above examples, to indicate the nature and magnitude of the charge. The fraction of the salt dissociated is called its *ionization* γ. This fraction always decreases with increasing concentration.

Prob. 1. A solution of 0.65 formula-weight KCl in 1000 g. water has at 100° a vapor-pressure of 744.8 mm. Calculate the number of mols of solute per formula-weight of salt and the ionization of the salt.

Prob. 2. According to an estimate based upon certain of its properties, sulphuric acid in a solution containing 0.05 formula-weights H_2SO_4 per 1000 g. water at 0° is 58% ionized into H^+ and HSO_4^- and 36% into H^+, H^+, and SO_4^{--}. Calculate the total number of mols of solute per formula-weight of the acid and the freezing-point of the solution. (The observed freezing-point is —0.215°.)

42

CONDUCTION OF ELECTRICITY IN SOLUTIONS: FARADAY'S LAW

41. Electrolytic Conduction.—Conductors are divided into two classes with reference to the changes that are produced in them by the passage of electric currents. Those which undergo no changes except such as are produced by a rise in temperature are called *metallic conductors*. Those in which the passage of a current is attended by a chemical change are called *electrolytes*. Aqueous solutions of salts, bases, and acids, and melted salts at high temperatures, are the most important classes of the well-conducting electrolytes. The most obvious chemical changes attending the passage of a current through an electrolyte are those that take place at the surfaces of the metallic conductors where the current enters and leaves the electrolyte. The production of such chemical changes by a current from an external source is called *electrolysis*. The occurrence of such changes, when they themselves give rise to an electric current, is called *voltaic action*. Those portions of the metallic conductors that are in contact with the electrolyte are called the *electrodes;* the one at which the current leaves the electrolyte, or the one towards which the positive electricity flows through the electrolyte, is designated the *cathode;* the other, the *anode*.

42. Chemical Changes at the Electrodes.— The chemical change produced at the cathode is always a reduction; that at the anode, an oxidation. The products resulting when aqueous solutions of certain typical salts, bases, and acids are electrolyzed between electrodes which are unattacked are as follows:

Solute	Cathode products	Anode products
$Cu(NO_3)_2$ or $AgNO_3$	Cu or Ag	O_2 and HNO_3
KNO_3	H_2 and KOH	O_2 and HNO_3
Na_2SO_4	H_2 and NaOH	O_2 and H_2SO_4
KOH or $Ba(OH)_2$	H_2	O_2
H_2SO_4 or H_3PO_4	H_2	O_2
Dilute HCl or HNO_3	H_2	O_2
Concentrated HCl	H_2	Cl_2
Concentrated HNO_3	NO_2 and NH_3	O_2

When the anode is a metal which can react with the anion of the solute, the change at the anode consists only in the dissolving of the metal; thus when a nitrate or sulphate is electrolyzed with a copper anode, copper passes into solution forming copper nitrate or sulphate.

In the case of voltaic actions, the chemical changes are of a

similar character, most commonly consisting in the solution of the metal composing the anode and in the deposition of another metal or of hydrogen on the cathode (the separation of free hydrogen being, however, often prevented by a secondary reaction between it and the electrolyte or the electrode). Thus, in the Daniell cell, which consists of a copper electrode in a copper sulphate solution and of a zinc electrode in a zinc sulphate solution, the two solutions being in contact and the two electrodes connected by a metallic conductor, the zinc dissolves and the copper precipitates; and, in the Grove cell, consisting of a zinc electrode in dilute sulphuric acid and a platinum electrode in strong nitric acid, zinc dissolves at the anode, and the hydrogen primarily produced at the cathode reduces the nitric acid to lower oxides of nitrogen. The chemical changes involved in voltaic actions do not differ, therefore, essentially from those produced by electrolysis.

Prob. 3. State what chemical change takes place at each electrode when electricity passes through: *a*, a concentrated solution of NaCl between a carbon anode and an iron cathode; *b*, a solution of NaCl between a silver anode and a metal cathode coated with AgCl; *c*, dilute H_2SO_4 between a lead anode and a cathode of lead coated with PbO_2; *d*, a solution of $ZnSO_4$ between a zinc-amalgam anode and a cathode of mercury covered with Hg_2SO_4.

43. Faraday's Law.—The passage of electricity through an electrolyte is attended at each electrode by a chemical change involving a number of chemical equivalents N strictly proportional to the quantity of electricity Q passed through and dependent on that alone. That is: $Q = F N$, where F is a constant with respect to all variations of the conditions, such as temperature, concentration, current-strength, current-density, etc. Such variations often influence the character of the chemical change, but not the total number of equivalents involved. The law is applicable to concentrated, as well as to dilute solutions, and to fused salts.

The constant F evidently represents the quantity of electricity producing a chemical change involving one equivalent. It is called a *faraday,* and has the value **96500** coulombs. One *coulomb* is the quantity of electricity flowing per second when the current is one *ampere.*

The term chemical equivalent in the above statement of Faraday's law signifies the oxidation or reduction equivalent of the substance,

in the sense in which it is used in volumetric analysis. That is, *one equivalent* of any substance is that weight of it which is capable of oxidizing one atomic weight of hydrogen, or which has the same reducing power as one atomic weight of hydrogen.

Prob. 4. Through solutions of $AgNO_3$, $AuCl_3$, Hg_2SO_4, and $HgCl_2$, placed in series, 9650 coulombs are passed. How many grams of metal will be deposited on the cathode from each solution?

Prob. 5. A Daniell cell, consisting of zinc in zinc sulphate solution and copper in copper sulphate solution, furnishes a current of 0.1 ampere for 100 minutes. How many grams of copper deposit and of zinc dissolve in the cell?

Prob. 6. How long must a current of 5 amperes be passed through dilute sulphuric acid in order to produce at 27° and 1 atm., *a*, one liter of oxygen? *b*, one liter of hydrogen?

Prob. 7. 1930 coulombs are passed through a solution of copper sulphate. At the cathode 0.018 equivalent of copper are deposited. How many equivalents of hydrogen are set free?

44. Relation of Faraday's Law to the Ionic Theory.—Faraday's law evidently shows that electricity is transported from solution to electrode, or in the reverse direction, only by the constituents of the electrolyte; and that one equivalent of any constituent carries the same quantity of electricity, namely, one faraday or 96500 coulombs. The dissociated portions of these constituents* are called *ions*—the positively charged ones *cations,* and the negatively charged ones *anions.* It is to be noted that the flow of current to the cathode may be brought about either by the deposition of a cation on the electrode or by the dissolving from the electrode of a substance that forms an anion; for flow of negative electricity in one direction produces a current having the same electrical effects as flow of positive electricity in the other.

Prob. 8. When one faraday is passed through a potassium sulphate solution, not only one equivalent of hydrogen, but also one equivalent of potassium hydroxide, is produced at the cathode; and not only one equivalent of oxygen, but also one equivalent of sulphuric acid, is produced at the anode. Show that these facts would not be in accord with Faraday's law if the ions were assumed to be $(K_2O)^{++}$ and $(SO_3)^{--}$, but that they are in accord with it if the ions are assumed to be K^+ and SO_4^{--}.

---

*The two ion-forming constituents themselves, considered without reference to the extent to which they may be dissociated from each other in the solution, will be hereafter called the *ion-constituents.* Thus the ion-constituents of potassium nitrate are K and NO_3, since its ions are K^+ and NO_3^-.

ELECTRICAL TRANSFERENCE

45. Phenomenon of Electrical Transference.—When a current is passed through a solution of a salt, base, or acid, in addition to the chemical changes taking place at the electrodes in accordance with Faraday's law, a certain quantity of the cation-constituent is transferred from the neighborhood of the anode to that of the cathode, and a certain quantity of the anion-constituent is transferred in the reverse direction. This phenomenon can best be made clear by the consideration of an actual transference determination. Consider, for example, that a 0.02 normal solution of sodium sulphate is electrolyzed at 18° in an apparatus like that shown in Figure 5, between a platinum cathode (marked —) and a platinum anode (marked +). To avoid stirring of the solution, the electrodes, from which hydrogen and oxygen gases are evolved, are placed near the surface; the anode, around which the solution becomes denser during the electrolysis, is placed near the bottom of the tube; and the apparatus is immersed in a water-bath kept at constant tem-

FIGURE 5

perature. The current is stopped before the electrode-products (the sodium hydroxide and sulphuric acid) have migrated beyond the dotted lines in the figure. The three portions of the solution (called the cathode-portion, middle-portion, and anode-portion, and marked C, M, and A, respectively) are then separately removed from the apparatus, and submitted to analysis. The quantity of sodium and of sulphate present in each portion is compared with the quantity of it originally associated with the weight of water contained in the portion. It is found, if the experiment has been successful, that the middle-portion has undergone no change in composition, that the cathode-portion has increased its sodium-content and decreased its sulphate-content, and that the anode-portion has increased its sulphate-content and decreased its sodium-content. It is found, per faraday of electricity passed through the solution, that the sodium-content has increased in the cathode-portion by 0.39 equivalent and has decreased in the anode-

portion by the same amount, and that the sulphate-content has increased in the anode-portion by 0.61 equivalent and has decreased in the cathode-portion by the same amount.
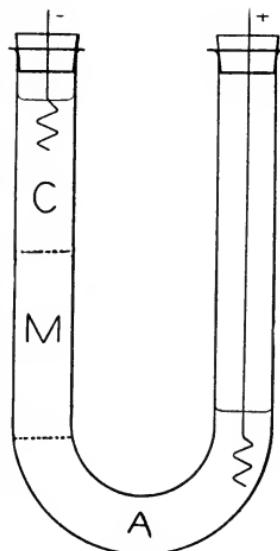
When either of the constituents whose transference is being determined is deposited on or dissolved off the electrode, as is the case when a silver-nitrate solution is electrolyzed between silver electrodes, the quantity of it so deposited or dissolved must evidently be determined either by direct weighing or by calculation with the aid of Faraday's law, and be subtracted from or added to the change in content of that constituent in the electrode-portion.

46. Law of Transference.—The sum of the number of equivalents of the cation and anion constituents (N_C and N_A) transferred in the two directions is equal to the number of faradays (N) passed through the solution. That is, $N_C + N_A = N$. This equation is illustrated by the data for sodium sulphate given above.

In the case of mixtures containing various ion-constituents ($C_1, C_2, \ldots A_1, A_2 \ldots$) all of these are transferred, and the expression of the law of transference is: $N_{C_1} + N_{C_2} \ldots + N_{A_1} + N_{A_2} \ldots = N$.

47. Transference-Numbers.—The equivalents N_C of cation-constituent transferred are in general not equal to the equivalents N_A of anion-constituent transferred. The experimentally determined ratios $N_C/(N_C + N_A)$ and $N_A/(N_C + N_A)$ are called the transference-numbers, T_C and T_A, of the cation and anion, respectively. These transference-numbers evidently represent (since $N_C + N_A = N$) the equivalents of cation or anion-constituent transferred per faraday. Thus in the case of sodium sulphate $T_C = 0.39$ and $T_A = 0.61$.

Prob. 9. Through a 0.2 normal solution of potassium sulphate between platinum electrodes 0.0075 faraday is passed at 25°. The cathode-portion after the electrolysis was found to contain 0.1450 g. more potassium than was originally associated with the weight of water in the portion. What is the transference-number of the sulphate-ion?

Prob. 10. A current is passed at 25° through a solution of 16.64 g. $Pb(NO_3)_2$ in 1000 g. water between lead electrodes until 0.1658 g. silver is deposited in a coulometer in series with it. The anode portion weighed 62.50 g. and yielded on analysis 1.123 g. $PbCrO_4$. What is the transference-number of the lead-ion? Assume that lead dissolves off the anode in accordance with Faraday's law.

Prob. 11. A current of 0.1 ampere is passed for 30 minutes through a 0.2 normal $Ba(NO_3)_2$ solution between platinum electrodes. The

transference-number for the barium-ion is 0.45. What changes, expressed in equivalents of the ion-constituents, result in the anode-portion and in the cathode-portion from the electrolysis? from the transference? What is the net result of these two effects on the quantities of the various compounds present in each portion?

48. Transference in Relation to the Ionic Theory. The Mechanism of Conduction in Solutions.—Just as Faraday's law shows that electricity is carried from the solution to the electrode only by the ion-constituents, so the law of transference ($N_C + N_A = N$) shows that through the solution the electricity is likewise carried only by the ion-constituents. The only difference is that as a rule only one kind of ion-constituent carries the electricity to the electrode, while all the ion-constituents present take part in the conduction of it through the solution.

That the ion-constituents do move through the solution can be shown by placing the solution of a salt, such as copper sulphate or potassium permanganate, whose cation or anion has a characteristic color, beneath a solution of a colorless salt, such as potassium sulphate, and applying a potential-difference at the electrodes.

The movement of the ion-constituents is explained by the ionic theory as follows. A certain fraction of the molecules of a salt exists in the state of positively and negatively charged molecules, called cations and anions. When a solution is placed between electrodes that are at different potentials, the ions in virtue of their charges are subjected to an electric force which drives them through the solution—the cations towards the cathode, the anions towards the anode; while the unionized molecules, being electrically neutral, are unaffected. The ions are, however, constantly uniting to form unionized molecules, and the latter are constantly dissociating into ions For this reason, although at any moment only the ions are moving, the resultant effect is that the ion-constituent as a whole moves continuously towards the electrode. The rate at which the ion-constituent moves is equal to the rate at which the ion moves multiplied by the ionization of the salt; for the statement that a certain fraction of the molecules is ionized is equivalent to the statement that any one molecule exists in the form of its ions during that fraction of the time.

49. Transference in Relation to the Mobility of the Ions. — The electric force f acting on any charged body is equal to its charge q multiplied by the potential-gradient; that is, $f = q(d_E/dl)$, where d_E is the change of potential in the distance dl. Moreover, the velocity of any body moving through a medium of great frictional resistance is proportional to the force acting upon it. Therefore, since the resistance to the motion of ions through solutions is very great, the velocity u of any given ion is proportional to the potential-gradient; that is: $u = u(d_E/dl)$, where u is the velocity under unit potential-gradient, called the *mobility* of the ion. The velocity of the ion-constituent is evidently also proportional to the potential-gradient.

Prob. 12. A solution containing c equivalents of a salt per ccm. of solution is placed in a cylindrical tube of cross-section q sqcm. between electrodes l cm. apart, at which a potential-difference E is applied. The mobilities of the cation and anion constituents in this solution are u_C and u_A, respectively. Sketch a diagram illustrating these conditions, and derive an expression for the number of equivalents N_C and N_A of the cation and anion constituents which migrate through any cross-section of the solution in the time t.

Since the migration considered in Prob. 12 takes place also through the cross-sections which separate the middle portion from the two electrode portions, it is evident that the equivalents of the cation and anion constituents transferred are to each other as their mobilities. That is, $N_C/N_A = u_C/u_A$; and therefore:

$$T_C = \frac{u_C}{u_C + u_A} \quad \text{and} \quad T_A = \frac{u_A}{u_C + u_A}.$$

It is also evident that the transference-number of either ion-constituent is the fraction of the current which is carried by that constituent.

Prob. 13. An ordinary transference determination is made at 18° with 0.1 normal $AgNO_3$ solution in a cylindrical tube 4 cm. in diameter between silver electrodes 30 cm. apart. Analysis of the anode-portion shows that 0.00207 equivalent of silver have migrated out of it. *a.* Calculate the distance through which the silver migrated during the passage of the current. *b.* The potential-difference applied at the electrodes was 10 volts, and the resulting current of 0.0395 ampere was passed for 3 hours. Calculate the mobility in centimeters per second of each of the ion-constituents. (Assume that the concentration-changes at the electrodes do not affect the potential-gradient.)

50. The Moving-Boundary Method of Determining Transference.
—The relation derived in Prob. 12 forms the principle of another
method of determining transference. In this method the
relative rates are measured at which the two boundaries
of a solution of a salt CA move when placed between
solutions of two other salts* C′A and CA′, arranged as
in Figure 6, in which $c\,c$ and $a\,a$ represent the original
positions of the boundaries, $c'\,c'$ and $a'\,a'$ their positions
after a certain time. It is evident that the cation-con-
stituent C moves the distance $c\,c'$ while the anion-con-
stituent A moves the distance $a\,a'$; and that they are
moving under the same potential-gradient, since they
are in the same solution. Therefore the ratio $c\,c'/a\,a'$ is
the ratio of the mobilities u_C/u_A, and hence of the transfer-
ence-numbers T_C/T_A.
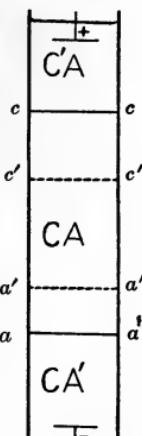
FIGURE 6

The boundaries are most readily seen when the "indicator" ions
C′ and A′ are colored; but even when the ions are all colorless, the
boundaries are usually visible because of the different refractive power
of the adjoining solutions.

Prob. 14. In a moving-boundary experiment an apparatus like that
represented by Figure 6 is charged at 18° with solutions of silver nitrate
at the bottom, of potassium nitrate in the middle, and of potassium
acetate at the top. The lower electrode, which is of silver, is made the
anode. In 90 minutes the lower boundary moves 3.00 cm. and the upper
boundary 2.88 cm. What transference-numbers can be derived from
these facts, and what are their values?

51. Change of Transference-Numbers with the Concentration.—
The transference-numbers of almost all uniunivalent and unibivalent
salts (except the halides of bivalent metals) remain sensibly constant
as the concentration increases, so long as it does not exceed a moder-
ate value, say 0.1 normal. For example, the values at 18° of the
sodium transference-number T_{Na} in sodium chloride solutions at vari-
ous concentrations c are as follows:

| T_{Na} | 0.396 | 0.396 | 0.395 | 0.393 | 0.388 | 0.369 |
| c | 0.005 | 0.020 | 0.050 | 0.100 | 0.300 | 1.000 normal. |

*In order that the boundaries remain sharp it is evidently necessary that
the ion C′ have a smaller velocity than the ion C, and that the ion A′ have a
smaller velocity than the ion A; for otherwise the ions C′ and A′ would enter the
solution of the salt CA, producing a mixture at each boundary.

The constancy of these numbers in the dilute solutions shows that the ratio of the velocities of the two ion-constituents does not vary, which might be expected to be true so long as they are moving through a medium which is substantially the same as pure water. At higher concentrations the transference-number often changes rapidly with increasing concentration. This may be due to a variety of causes. Thus it may arise from a change in the frictional resistance of the medium; from hydration of the ions, which causes water to be transferred and thus affects the transference value, since this is computed under the assumption that the water is stationary; from existence of complex ions, which in concentrated solutions are more likely to be present in considerable quantity.

52. Determination of the Composition of Ions by Transference Experiments.

Prob. 15. When one faraday is passed through a solution of potassium silver cyanide (KCN.AgCN) the cathode-portion loses 1.40 equivalents of silver and 0.80 equivalent of cyanogen, and gains 0.60 equivalent of potassium. Explain what this shows in regard to the composition of the ions and their transference-numbers.

Prob. 16. A transference experiment is made by passing 0.01 faraday through a solution 0.2 formal in $AgNO_3$ and 0.6 formal in NH_3 between silver electrodes at 18°. The anode-portion is found to gain 0.0053 equivalent of silver and to lose 0.0094 formula-weight NH_3. Explain what this shows in regard to the composition of the ions. (Silver dissolves at the anode in accordance with Faraday's law.)

Prob. 17.—Determination of the Hydration of Ions.—In a transference experiment 0.0525 faraday was passed at 25° through a solution placed between silver electrodes and containing 1.12 formula-weights of NaCl and 0.073 formula-weights of raffinose ($C_{18}H_{32}O_{16}$) in 1000 g. of water. The anode-portion was found by analysis to contain 0.72 g. less water and 1.115 g. less NaCl than was originally associated with the raffinose present in that portion. *a.* Calculate the number of mols of water and the number of equivalents of sodium transferred per faraday from the anode to the cathode, assuming that the raffinose does not migrate. *b.* Assuming no hydration of the chloride ion, calculate the number of molecules of water associated with the atom of sodium in the sodium ion. *c.* Assuming the chloride ion is hydrated with x molecules of water, calculate the hydration of the sodium ion.

Note.—Similar experiments made with other halides have given the following values for the number of molecules of water contained in other ions, assuming the number in the chloride ion to be x molecules:

H^+ : $0.28 + 0.185x$. K^+ : $1.3 + 1.02x$.

Cs^+ : $0.67 + 1.03x$. Li^+ : $4.7 + 2.29x$.

ELECTRICAL CONDUCTANCE

53. Conductance, Specific Conductance, and Equivalent Conductance.—According to Ohm's law, the current I flowing between two points of a conductor is proportional to the potential-difference E at those points. The ratio of the current to the potential-difference is called the *conductance* L; and the inverse ratio, the *resistance* R. That is,

$$I/E = L, \text{ and } E/I = R.$$

When the current is expressed in amperes and the potential difference in volts, the resistance is in ohms and the conductance in reciprocal ohms. An *ohm* is the resistance, and a *reciprocal ohm* the conductance, of a column of mercury at 0° one square millimeter in cross-section and 106.3 centimeters long.

The conductance of a homogeneous body of uniform cross-section is proportional to its cross-section q and inversely proportional to its length l. That is, $L = \bar{L} q/l$. The proportionality-factor $\bar{L}$, which is the conductance when the cross-section is one square centimeter and the length one centimeter, is called the *specific conductance*. Its reciprocal is called the *specific resistance*.

In the case of a salt in solution, the term *equivalent conductance* Λ is employed to denote the conductance of that volume of solution which contains one equivalent of salt, when placed between parallel electrodes one centimeter apart. Thus the equivalent conductance $\Lambda_{0.1}$ of a salt in 0.1 normal solution represents the conductance of 10,000 cubic centimeters of that solution when placed between parallel electrodes one centimeter apart.

The equivalent conductance of dissolved salts increases with decreasing concentration at first rapidly, then more slowly, and approaches a maximum value as the concentration approaches zero. This is illustrated by the following data at 18°:

Equiv. per liter....	1	0.1	0.01	0.001	0.0001	0.0
Λ for NaCl........	74.4	92.0	102.0	106.5	108.1	109.0
Λ for K_2SO_4.......	71.6	94.9	115.8	126.9	130.8	133.0

The equivalent conductance of largely ionized solutes increases with rising temperature. At 18° the increase in dilute solution is from 2.1 to 2.5% per degree in the case of salts, and about 1.6% per degree in the case of strong acids.

Prob. 18. What is the specific conductance in reciprocal ohms of mercury at 0°?

Prob. 19. a. Derive the algebraic relation expressing equivalent conductance in terms of specific conductance and concentration in equivalents per cubic centimeter. *b.* Calculate the specific conductance of the sodium chloride solutions whose equivalent conductances are given above.

Prob. 20. A 0.1 normal solution of silver nitrate at 18° is placed in a tube 4 cm. in diameter between silver electrodes 12 cm. apart. A potential difference of 20 volts at the electrodes produces a current of 0.1976 ampere. Calculate the conductance, the specific conductance, and the equivalent conductance of the solution.

Prob. 21. The equivalent conductance of a 0.01 normal $CuSO_4$ solution at 18° is 71.7 reciprocal ohms. What is the resistance of a column of it 20 cm. long and 5 sqcm. in cross-section?

54. Relation of Conductance to the Mobility of the Ion-Constituents.

Prob. 22. In 0.2 normal $NaNO_3$ solution the mobility at 18° of the sodium is 0.000505 and that of the nitrate 0.000356 cm. per second. Calculate the conductance of a column of the solution 10 cm. long and 2 sqcm. in cross-section. Note that the conductance of any conductor is the quantity of electricity in coulombs which passes per second when the potential-difference at the ends is 1 volt; and that the conductance of a salt solution is the sum of the conductances of its two ion-constituents.

Prob. 23. Show that the specific conductance $\bar{L}$ and equivalent conductance Λ are expressed by the equations:

$$\bar{L} = \bar{L}_C + \bar{L}_A = (U_C + U_A) \, F \, c, \quad \text{and} \quad \Lambda = \Lambda_C + \Lambda_A = (U_C + U_A) \, F,$$

where c is the concentration in equivalents per cubic centimeter of a solution in which the mobilities of the ion-constituents are U_C and U_A.

55. Relation of Equivalent Conductance to Ionization.—The

equation $\Lambda = (U_C + U_A) \, F$ shows that the observed increase of equivalent conductance with decreasing concentration is due to an increase in the mobilities of the ion-constituents. In the case of dilute solutions of di-ionic substances this increase in mobility doubtless arises, in the way described in Art. 48, from a proportionate increase in the ionization of the substance; for up to moderate concentrations the resistance to the movement of the ions is presumably the same as in pure water. The maximum value attained at zero concentration evidently corresponds to complete ionization. The ratio of the equivalent conductance Λ at any, not too high, concentration to the equivalent

conductance Λ_0 at zero concentration is therefore equal to the ioniza-tion γ in the case of a di-ionic substance. That is, $\Lambda / \Lambda_0 = \gamma$. The Λ_0-value is ordinarily obtained by extrapolation. When the substance is completely ionized the mobilities U_C and U_A and equivalent con-ductances Λ_C and Λ_A of the two ion-constituents become identical with those, U_{C^+}, U_{A^-}, Λ_{C^+}, Λ_{A^-}, of the corresponding ions. Therefore $\Lambda_0 = \Lambda_{C^+} + \Lambda_{A^-} = (U_{C^+} + U_{A^-})$ F. These *ion-mobilities* and *ion-conductances* have at each temperature a certain value for each ion, whatever be the other ion in the solution.

Prob. 24. In 0.1 normal solution at 18°, HCl and $HC_2H_3O_2$ are 92% and 1.35% ionized, respectively. With what velocity in centimeters per hour does the hydrogen migrate through each solution when the potential-gradient is 10 volts per centimeter? The mobility of the hydrogen-ion at 18° is 0.00326 cm. per second.

Prob. 25. At 18° the equivalent conductance of 0.1 normal NH_4OH is 3.1 reciprocal ohms. The equivalent conductance at zero concentra-tion for NH_4Cl, KCl, and KOH is 130.2, 130.0, and 239 reciprocal ohms, respectively. What is the ionization of ammonium hydroxide in 0.1 normal solution?

The determination of the ionization of polyionic substances is complicated, even in dilute solutions, by the fact that these substances dissociate in two ways; thus sulphuric acid dissociates partially into H^+ and HSO_4^-, and partially into H^+, H^+, and SO_4^{--}. The conductance-ratio for such substances has therefore no simple significance.

In even moderately concentrated solutions the frictional resistance to the motion of the ions must be appreciably different from that in pure water; and the conductance-ratio Λ / Λ_0 cannot therefore be an exact measure of the ionization. An approximate estimate of the variation of this frictional resistance is given by the ratio of the vis-cosity η of the solution to the viscosity η_0 of pure water at the same temperature. This viscosity-ratio η / η_0 is determined by measuring the relative times required for equal volumes of the solution and of pure water to flow through the same capillary tube, when subjected to the same pressure. A film of the liquid adheres firmly to the walls of the tube; and the phenomenon of the flow consists essentially in the slipping of the successive cylindrical shells of liquid past one another. Viscosity is therefore a property which depends on the frictional re-sistance to the motion of the molecules of the liquid past one another; and it may be expected to be roughly proportional to the frictional

resistance to the motion of ions through the same liquid. By taking the viscosity into account an ionization-value can be derived which is more accurate than that given by the conductance-ratio alone.

Prob. 26. a. At 18° the viscosities of 0.1-normal and 1.0-normal NaCl solutions are respectively 1.009 and 1.086 times as great as that of pure water. With the aid of these data and those given in Art. 53 calculate the ionization of NaCl at 18° at these two concentrations. *b.* Formulate an algebraic expression for the ionization in terms of the conductances and viscosities.

Note.—The viscosity-ratios η / η_0 for some other salts at 18° at 1-normal are as follows:

Salt	KCl	LiCl	$MgCl_2$	K_2SO_4	$MgSO_4$
η / η_0	0.982	1.150	1.213	1.101	1.381

The deviation of the ratio from unity at 0.1-normal is approximately one-tenth of that at 1-normal.

56. Mobility and Conductance of the Separate Ions.—Although only the sum of two ion-conductances is given by the Λ_0-value, the conductances of the separate ions may be obtained by combining it with the transference-number.

Prob. 27. a. Calculate from the conductance and transference data given in Arts. 51 and 53 for sodium chloride the equivalent conductances of sodium-ion and chloride-ion. *b.* At 18° the value of Λ_0 for KCl is 130.0, for KNO_3 is 126.3, and for HNO_3 is 377 reciprocal ohms. From these data and the result obtained in *a*, calculate a value for the equivalent conductance of each of the ions of these salts. *c.* Calculate the cation-transference-number at 18° for nitric acid in dilute solution. (The experimentally found value is 0.839 at 0.005 normal.)

The following table contains the values of the equivalent conductance Λ of some important ions at 18°, and the values of its fractional increase $\propto$ (equal to $(d\Lambda/\Lambda)/dT$) with the temperature at 18°.

	Λ	$\propto$		Λ	$\propto$
H^+	315	0.0154	OH^-	174	0.0180
Li^+	33.3	265	F^-	46.7	238
Na^+	43.4	244	Cl^-	65.5	216
K^+	64.5	217	Br^-	67.7	215
NH_4^+	64.7	222	I^-	66.6	213
Ag^+	54.0	229	NO_3^-	61.8	205
Mg^{++}	45.9	256	ClO_3^-	55.1	215
Ca^{++}	51.9	247	BrO_3^-	47.6	216
Ba^{++}	55.4	238	IO_3^-	34.0	234
Pb^{++}	60.8	243	$C_2H_3O_2^-$	35.	238
Cu^{++}	45.9	254	SO_4^{--}	68.5	227
Zn^{++}	47.0	254	$C_2O_4^{--}$	63.0	220

Prob. 28. *a.* From a consideration of the table given in the preceding text state the relation that exists between the ion-conductances and the atomic weights of the different elementary ions belonging to the alkali group and to the alkaline-earth group. *b.* Suggest an explanation of this apparently anomalous phenomenon. *c.* The viscosity of water at 18° decreases 2.6% per degree. State and explain any relation that this value has to the temperature-coefficients of the ion-conductances.

From these ion-conductances the Λ_0-value for the various salts can be obtained by simple addition. This fact is of especial importance in the case of substances for which the Λ_0-value cannot be obtained from conductance measurements by extrapolation. This is true of weak bases and acids, such as ammonium hydroxide and acetic acid, whose ionization is far from complete even in dilute solution, and of salts, such as ammonium acetate, which are appreciably hydrolyzed in dilute solution.

From the ion-conductances can be calculated also the specific conductance of any solution in which the ion-concentrations are known.

Prob. 29. In a solution at 18° containing 0.10 equivalent NaCl and 0.05 equivalent KCl, each of the salts is 82% ionized. Calculate the ion-concentrations, and from them the specific conductance of the solution.

57. Ion-Concentrations Derived from Conductance Measurements.

*Prob. 30.—Determination of the Solubility of Slightly Soluble Substances.—*When water at 18° is saturated with silver chloride, its specific conductance increases by 1.25×10^{-6} reciprocal ohm. Assuming that the silver chloride is completely ionized, find its solubility in equivalents per liter.

Prob. 31. At 25° the specific conductance of pure water due to its ionization into H^+ and OH^- is 0.055×10^{-6} reciprocal ohm. What is the concentration of these ions in equivalents per liter? (In calculating the ion-conductances at 25°, use the temperature-coefficients given in the above table.)

THE IONIZATION OF SUBSTANCES OF DIFFERENT TYPES

58. Ionization of Substances as Derived from the Conductance-Ratio.—Almost all salts (but not acids or bases) of the same valence type (*i. e.*, those whose ions have the same electric charge or valence) have at the same concentration and temperature not far from the same value of the ratio $\Lambda\eta / \Lambda_0\eta_0$. The average values of this quantity at 18° for the three simplest types of salts are as follows:

Type	Example	0.001	0.01	0.02	0.05	0.1 normal
Uniunivalent	KNO_3	0.98	0.93	0.91	0.87	0.84
Unibivalent	$\begin{Bmatrix} BaCl_2 \\ K_2SO_4 \end{Bmatrix}$	0.95	0.87	0.84	0.78	0.73
Bibivalent	$MgSO_4$	0.86	0.64	0.56	0.47	0.41

Few salts of the uniunivalent or unibivalent type have ratios at 0.1 normal differing by more than five per cent. from the average values given above. There are, however, certain salts of the unibivalent type which form marked exceptions to the rule; thus at 0.1 normal the ratio for cadmium chloride is 45%, and the ratios for the three mercuric halides are all less than 0.1%. The value of the ratio for all the types of salts decreases with rising temperature, but only to a slight extent.

It has already been stated in Art. 55 that the ratio $\Lambda\eta / \Lambda_0\eta_0$ is approximately equal to the ionization up to fairly large concentrations in the case of uniunivalent substances. In the case of unibivalent substances this is not true, owing to the fact that they ionize partially in two ways—with formation of the intermediate ion as well as with formation of the ultimate ions to which the Λ_0-value corresponds. In the case of salts of this unibivalent type the proportion of the intermediate ion present is not accurately known; up to concentrations of 0.1–0.2 normal it is, however, so small that only a small error results from neglecting it in calculating from the ratio $\Lambda\eta / \Lambda_0\eta_0$ the concentration of the ultimate univalent ion; but a much larger error results in thus calculating the concentration of the bivalent ion.

Prob. 32. At 18° the specific conductance of a 0.05 formal K_2SO_4 solution at 18° is 0.00949. *a.* Formulate an expression for this specific conductance in terms of the equivalent concentrations and conductances of the three kinds of ions that may be present. *b.* Calculate with the aid of this expression the equivalent concentrations of K^+ and of SO_4^{--}, assuming that these are the only ions present. *c.* Calculate these equivalent concentrations, assuming that 20% of the salt is ionized into KSO_4^-

and K^+, and that the equivalent conductance of KSO_4^- is 35. *d.* Tabulate for cases *b* and *c* the fraction of the total sulphate which exists as SO_4^{--}, KSO_4^-, and K_2SO_4, respectively.

Acids and bases, unlike salts, exhibit at any moderate concentration, such as 0.1 normal, every possible degree of ionization between a small fraction of one per cent. and 90 to 95%. There is, to be sure, a fairly large group of monobasic acids and monacidic bases, including HCl, HBr, HI, HNO_3, $HClO_3$, KOH, NaOH, LiOH, which have ionization-values comparable with those of the uniunivalent salts. with which therefore they may be classed. But outside of this group all possible values are met with, as illustrated by the following values of the percentage ionization $(100\,\gamma)$ at $25°$ and 0.1 formal: H_2SO_3, 34% (into H^+ and HSO_3^-); H_3PO_4, 28% (into H^+ and $H_2PO_4^-$); HNO_2, 7%; $HC_2H_3O_2$, 1.3%; H_2CO_3, H_2S, HClO, HCN, HBO_2, all less than 0.2%.

Polybasic acids are known to ionize in stages, giving rise to the intermediate ion; and the first hydrogen is almost always much more dissociated than the second, and the second much more than the third. Thus H_2SO_3 at 0.1 normal at $25°$ is about 34% dissociated into H^+ and HSO_3^-, and less than 0.1% dissociated into H^+ and SO_3^{--}. Methods by which the dissociation of the successive hydrogens can be determined will be referred to in Art. 84.

59. Comparison of Ionization-Values Derived from the Conductance-Ratio and from the Freezing-Point-Lowering. — It has been shown that the ionization of substances can be determined with the aid of two entirely distinct principles. One of these, based on the increase in the number of mols produced by ionization, involves the assumption that the ions and unionized substance have the normal effect on the vapor-pressure and related properties of the solvent. The other principle, according to which the ionization is equal to the conductance-ratio, assumes that the decrease in the mobility of the ion-constituents with increasing concentration is due solely to the decrease in ionization of the substance. A comparison shows that the ionization-values derived in these two ways agree with each other within 2 or 3% in the case of most uniunivalent substances up to 0.1 normal.

The comparison of the ionization-values obtained by the two methods in the case of unibivalent salts is of complicated significance because of the presence of the intermediate-ion.

Prob. 33 a. Calculate the number of mols per formula-weight of K_2SO_4 in a 0.05 formal solution of it at 18° from the results obtained in Prob. 32 (under the two assumptions that the salt ionizes without formation of the intermediate ion and that it ionizes with formation of 20% of that ion). *b.* State how the number of mols per formula-weight of salt actually present in this K_2SO_4 solution could be experimentally determined.

REVIEW OF THE IONIC PROPERTIES OF SOLUTIONS

60. Review Problems.

Prob. 34. Give an expression for the transference-number in terms (*a*) of the number of equivalents transferred; (*b*) of the mobilities of the ion-constituents; (*c*) of the conductances of the ions.

Prob. 35. Express algebraically the relations (*a*) between resistance, conductance, specific conductance, and equivalent conductance; (*b*) between specific conductance and ion-mobilities.

Prob. 36. Calculate the number of equivalents of sodium that would be transferred per faraday from the anode to the cathode portion if the solution named in Prob. 30 were electrolyzed.

Prob. 37. What changes in the hydrogen, chlorine, and platinum content, expressed in terms of the number of atomic weights of each element, take place in the cathode portion when 4825 coulombs are passed through a solution of chlorplatinic acid (H_2PtCl_6) at 25°? Assume that this acid dissociates only into H^+ and $PtCl_6^{--}$ ions, whose equivalent conductances at 25° are 350 and 68, respectively. The cathode process consists only in the deposition of platinum.

Prob. 38. Sulphuric acid in 0.05 formal solution at 25° consists of 6% H_2SO_4, 67% HSO_4^-, 27% $SO_4^=$, and the corresponding amount of H^+. The equivalent conductances at 25° of H^+, HSO_4^-, and SO_4^{--} are 350, 35, and 80, respectively. *a.* Calculate the specific conductance of the solution at 25°. *b.* Calculate the change in the equivalents of hydrogen in the cathode portion when one faraday is passed. (Note that hydrogen is transferred both in the form of H^+ and of HSO_4^- ions.)

CHAPTER V

THE RATE OF CHEMICAL REACTIONS

THE EFFECT OF CONCENTRATION

61. Definition of Reaction-Rate.—The rate of a chemical reaction between gaseous or dissolved substances may be defined to be the number of equivalents of each of the reaction-products produced per liter in an infinitesimal time divided by that time; that is, the reaction-rate is dc/dt, where dc signifies the increase of the equivalent concentration of each of the reaction-products in the time dt. As to the significance of the terms *equivalent* and *equivalent concentration* see Arts. 4 and 27. It is in some cases simpler, especially in dealing with reactions between gases or with reactions that take place in stages, to employ molal concentration (c) in place of equivalent concentration (c); but when this is done it will be so specified.

Prob. 1. Sodium hydroxide and methyl acetate in dilute solution react with each other (forming sodium acetate and methyl alcohol) at a rate which at any moment is proportional to the concentration of the sodium hydroxide and to the concentration of the methyl acetate at that moment. At 25° in a solution 0.01 normal in each of these substances the rate at which sodium acetate is produced is at the start 0.00118 equivalents per liter per minute. What will be the concentration of the sodium acetate after 10 minutes?

62. The Law of Concentration-Effect.—The rate of any chemical reaction which takes place between perfect gases or perfect solutes at a constant temperature completely in one direction is proportional to the concentration of each of the reacting substances at the moment in question.

This law is exact only for perfect gases or perfect solutions; but, like the other limiting laws, it holds true approximately up to moderate concentrations. The statement of the law here given is a provisional one which will be made more complete after the mechanism of reactions has been considered.

Prob. 2. Express this law in the form of a differential equation for the general case that any number of substances A, B, C, . . . react with one another. Represent by c_{0A}, c_{0B}, c_{0C} . . . the concentrations of the reacting substances at time zero, and by c the concentration of the reaction-products which has resulted at any time *t*.

The proportionality-constant which occurs in the equation expressing the law of concentration-effect is called the *specific reaction-rate* (*k*). It evidently represents the rate which the reaction would have, under the assumption of proportionality, if the concentrations of all the reacting substances were unity (one equivalent per liter).

63. Reactions of the First Order.—The expression for the reaction-rate is simplest in the case of reactions in which only one substance undergoes a change in concentration. Such reactions, whose rate is expressed by a differential equation of the first degree, are called *reactions of the first order.*

Prob. 3. Cane-sugar in a dilute aqueous solution containing hydrochloric acid undergoes hydrolysis according to the reaction:

$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6(\text{glucose}) + C_6H_{12}O_6(\text{fructose}).$$
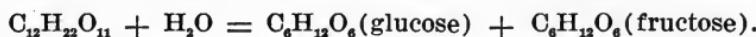
Formulate the differential equation expressing the rate at which the hydrolysis takes place.

Note.—In this case the concentration of the water does not change appreciably, since it is present in such large excess; and the concentration of the acid does not change at all, since it acts catalytically, accelerating the reaction without being consumed by it. It is not usual in formulating the reaction-rate equation or in evaluating the specific reaction-rate to take into account the concentrations of substances which, like these just mentioned, do not change with the progress of the reaction.

Prob. 4. Integrate the equation obtained in Prob. 3 between the time limits $t = 0$ and $t = t$ and the corresponding concentration limits.

Prob. 5. In a solution at 48° containing 0.3 mol of cane-sugar in a liter of 0.1 normal HCl, it is found (by measuring with a polarimeter the change in the optical rotatory power) that 32% of the sugar is hydrolyzed in 20 minutes. *a.* Calculate the specific reaction-rate and the actual rates at the beginning and at the expiration of 20 minutes. *b.* Calculate the percentage of sugar that will be hydrolyzed in 40 minutes. *c.* Calculate the percentage of sugar that would be hydrolyzed in 20 minutes, if 0.3 mol were dissolved in 10 liters (instead of 1 liter) of 0.1 normal HCl.

64. Reactions of the Second and Third Orders.

Prob. 6. a. Formulate the differential equation expressing the rate in dilute solution of the reaction between two substances A and B.

b. Integrate this equation between the time limits $t = 0$ and $t = t$ for the case that the initial concentrations of the two substances have the same value c_0. Integrate the equation (with the aid of a table of integrals, if preferred) also for the case that the initial concentrations c_{0A} and c_{0B} are different from each other.

A reaction whose rate is expressed by the differential equation formulated in Prob. 6 is called a reaction of the second order. And in general, the *order* of a reaction is said to be equal to the degree of the differential equation expressing its rate.

The expressions for a reaction of a third order (between three substances A, B, and C) can be similarly derived. For the case that the three substances have the same initial concentration c_0 the integrated expression is: $\dfrac{1}{(c_0 - c)^2} - \dfrac{1}{c_0^2} = 2 k t$.

Prob. 7. When 0.01 mol of methyl acetate is dissolved at 25° in 1 l. of 0.01 normal NaOH, 11.8% of the ester is decomposed per minute at the start according to the reaction: $CH_3Ac + NaOH = NaAc + CH_3OH$. *a.* How long will it take for one half of the ester in this mixture to be saponified? *b.* How long will it take when 0.01 mol is dissolved in 1 liter of 0.02 normal NaOH? *c.* Suggest an analytical method by which the rate of this reaction could be followed experimentally.

65. Expressions of the Law of Concentration-Effect in Terms of the Fraction of the Reacting Substances Transformed.

Prob. 9. From the integrated expressions of the first, second, and third orders already obtained derive the expressions:

$$\log \frac{1}{1 - x} = k t; \quad \frac{x}{1 - x} = k t \frac{N_0}{v}; \quad \text{and} \quad \frac{x(2 - x)}{(1 - x)^2} = 2 k t \frac{N_0^2}{v^2},$$

in which x represents the fraction of the reacting substances transformed, v the volume of the mixture, and N_0 the equivalents of each of the reacting substances present at the start.

Prob. 10. Show from the expressions derived in Prob. 9 how the specific reaction-rate is related to the time required for the transformation of any definite fraction of the reacting substances in the case of different reactions of the same order, or of the same reaction at different temperatures.

Prob. 11. At 25° the specific rate of the reaction between sodium hydroxide and methyl acetate is 1.8 times as great as that of the reaction between sodium hydroxide and ethyl acetate. What is the ratio of the times required for decomposing 90% of the two esters when equivalent quantities are present at the start?

Prob. 12. What is the ratio of the times required for decomposing: *a*. 90% of 1 mol of cane-sugar when it is dissolved in 1 l. and in 10 l. of 0.1 normal HCl solution? *b*. 90% of 1 mol of methyl acetate when it is dissolved in 1 l. of normal NaOH solution and in 10 l. of 0.1 normal NaOH solution?

66. The Mechanism of Reactions. Influence of the Number of Molecules Involved.—The rate of certain reactions, such as:

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4, \text{ and}$$

$$2AgAc + NaCHO_2 = 2Ag + CO_2 + HAc + NaAc,$$
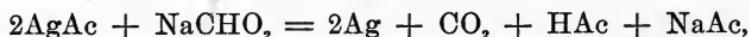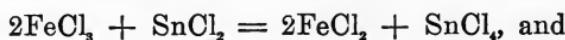
in which two molecules of one of the substances are involved, has been found to be proportional to the square (instead of to the first power) of the concentration of that substance. In other words, it is found that these reactions are of the third order, instead of the second order. The view that the number of reacting molecules determines the law of the rate is further substantiated by the fact that it harmonizes the law of reaction-rate with the well-established law of chemical equilibrium (see Prob. 26). These considerations justify the conclusion that the provisional statement of the law of concentration-effect should be modified so as to state that the rate is proportional to the concentration of each of the reacting substances raised to a power equal to the number of its molecules which interact with the molecules of the other substance in the ultimate molecular process on which the occurrence of the reaction depends. Thus, in the case of a reaction $aA + bB + cC = \ldots$, whose occurrence requires the interaction of a molecules of A, b molecules of B, c molecules of C, the general *law of concentration-effect* is expressed by the equation:

$$\frac{dc}{dt} = k \, (c_{0A} - c)^a \, (c_{0B} - c)^b \, (c_{0C} - c)^c \cdots$$

Prob. 13. Equal volumes of 0.2 normal solutions of silver acetate and sodium formate were mixed at 100°; and after definite intervals of time samples were removed and the undecomposed silver acetate was titrated with potassium thiocyanate. Its concentration was found to be 0.067 normal after 2 minutes, 0.047 normal after 6 minutes, and 0.032 normal after 14 minutes. Show from these data that this reaction conforms more closely to the expression of the third order than to that of the second order.

It is found, however, that many reactions which apparently involve three or more molecules conform to the expression of the second order. This is probably to be explained by the assumption that

the reaction expressed by the usual chemical equation takes place in stages, and that the stage which requires appreciable time is a reaction between two molecules. Thus the second-order reaction $H_2O_2 + 2HI = 2H_2O + I_2$ may be considered to take place in the two stages, $H_2O_2 + HI = H_2O + HIO$, and $HIO + HI = H_2O + I_2$; the first requiring a measurable time, and the second taking place almost instantaneously as soon as any HIO is formed by the first reaction. It is therefore necessary in the case of complex reactions to know their mechanism (the molecular process by which they take place), in order to predict the law of their rate; and conversely, the law of the reaction-rate throws light on the mechanism of the reaction.

Prob. 14. a. Suggest an explanation of the fact that the rate of the reaction $H^+BrO_3^- + 6H^+I^- = H^+Br^- + 3I_2 + 3H_2O$ is proportional to the first power of the concentration of the BrO_3^- and of that of the I^-. *b.* Explain also the fact that the decomposition of arsine gas, $4AsH_3 = As_4 + 6H_2$, is a reaction of the first order.

A knowledge of the mechanism of reactions is often important in other ways. Thus, the initial rates* at which an ester is decomposed by different bases of the same concentration are found to be proportional to the degrees of ionization of the bases, showing that it is the hydroxide-ion which is directly involved in the reaction; and this knowledge makes it possible to calculate the rate of decomposition of an ester by any solution whose hydroxide-ion concentration is known, or to make the converse calculation.

Prob. 15. At 25° the initial rate of decomposition of ethyl acetate by 0.01 normal NaOH is 9.0 times as great as that by 0.1 normal KCN. The sodium hydroxide is 96% ionized. What is the concentration of hydroxide-ion in the potassium cyanide solution?

*The initial rates have to be considered for the reason that the neutral salt which is produced as the reaction progresses has a great influence on the ionization of slightly ionized bases, as will be explained in the next chapter.

THE EFFECT OF CATALYZERS

67. Catalysis and Catalyzers.—A reaction is often greatly accelerated by the presence of a substance which is not itself consumed by the reaction. This phenomenon is called *catalysis,* and the substance producing it is called the *catalyzer.*

Although few general principles relating to catalysis have been established, its great practical importance makes it desirable to consider the more common types of catalyzers and the ways in which they act. This is done in Arts. 68–72.

68. Carriers.—Carriers constitute one of the most common and best understood types of catalyzers. The mechanism of their action is as follows: The catalyzer produces with one of the substances an intermediate compound which reacts with the second substance in such a way as to regenerate the catalyzer; the reaction of the second substance with the intermediate compound taking place more rapidly than that with the first substance. In this way a reaction which does not take place directly at an appreciable rate may be made to take place in stages at a rapid rate. The chamber process of making sulphuric acid and the technical method of making ether are familiar examples of this type, the fundamental reactions being:

$a.$ $O_2 + 2NO = 2NO_2$, and $SO_2 + NO_2 + H_2O = H_2SO_4 + NO$.

$b.$ $C_2H_5OH + H_2SO_4 = C_2H_5HSO_4 + H_2O$, and

$C_2H_5OH + C_2H_5HSO_4 = (C_2H_5)_2O + H_2SO_4$.

69. Contact Agents.—Reactions between gases or solutes are often greatly accelerated by placing the reacting mixture in contact with a suitable solid substance which offers a large surface. The heavier metals are especially likely to be effective; but many other substances have specific effects on definite reactions. The platinum contact-process of making sulphur trioxide from sulphur dioxide and oxygen and the Deacon process of making chlorine by passing hydrogen chloride and oxygen over a porous mass impregnated with copper chloride are examples of contact catalysis. Gas reactions are often catalyzed by solid surfaces to such an extent that the chemical change takes place appreciably only in the gas that is in immediate contact with the walls of the containing vessel or with solid material with which it may be charged.

The mechanism of contact actions is little understood. In most

cases, the contact action is probably due to an adsorption of the reacting substances (that is, to a concentration of them on the surface of the solid) and to the fact that in the surface-layer the reaction-rate is greatly increased. Thus, finely divided platinum placed in contact with illuminating gas and air adsorbs a large quantity of the gases, and these then react so rapidly as to cause the gas to take fire.

To reactions brought about by a contact agent the law of concentration-effect is, in general, not applicable; for the rate of such reactions must evidently be influenced by the rates at which the reacting substances are adsorbed by the solid surface.

70. Hydrogen-Ion and Hydroxide-Ion as Catalyzers.—In aqueous solutions many reactions are accelerated by hydrogen-ion. This is probably true of all reactions in which water is directly involved, such as the hydrolysis of cane-sugar or of esters. It is also true of certain reactions of oxidation and reduction.

The rate of such hydrolytic reactions in very dilute solutions is found to be proportional to the concentration of the hydrogen-ion; for example, the specific reaction-rate of the cane-sugar hydrolysis at 48° has been found to be 9.95 times as great in 0.01 normal HCl as it is in 0.001 normal HCl, while the ratio of the hydrogen-ion concentrations in the two solutions is 9.8. At higher hydrogen-ion concentrations or in the presence of neutral salts considerable deviations from proportionality exist; thus, the rate of the cane-sugar hydrolysis is 10.5 times as great in 0.1 normal HCl as in 0.01 normal HCl, while the hydrogen-ion concentration is only 9.5 times as great.

This principle can be employed (as shown by Prob. 18) for determining the hydrogen-ion concentration in solutions; for no other ion (except hydroxide-ion in certain cases) exerts a catalytic effect on hydrolytic reactions.

Reactions in which water takes part are often accelerated also by hydroxide-ion; thus, milk-sugar, $C_{12}H_{22}O_{11}$, dissolved in water becomes hydrated (with formation of $C_{12}H_{22}O_{11}.H_2O$) at a rate which is greatly increased by hydroxide-ion.

Prob. 16. Name two or three other reactions, besides those here referred to, which are accelerated by hydrogen-ion. Refer, if necessary, to chemical text-books.

Prob. 17. Show how the catalytic effect of hydrogen-ion on hydrolytic reactions may be interpreted as a carrier action, assuming that the hydrogen-ion is hydrated.

Prob. 18. Diazoacetic ester decomposes in aqueous solution according to the equation $CHN_2.CO_2C_2H_5 + H_2O = CH_2OH.CO_2C_2H_5 + N_2$, and the reaction is catalyzed by hydrogen-ion. At 25° in a solution 0.1 normal in acetic acid, whose ionization is 1.34%, 37.5% of the ester is decomposed in 10 minutes. Assuming that it takes 67 minutes to decompose the same percentage of the ester in a solution 0.1 formal in sodium hydrogen tartrate, what is the hydrogen-ion concentration in that solution?

71. Enzymes.—Certain complex organic substances called enzymes, which are produced by animal and plant organisms, have an extraordinary power of catalyzing certain organic reactions. The effect is highly specific, a particular enzyme being required for a particular reaction. Thus invertase, an enzyme produced by yeast, causes the conversion of cane-sugar into glucose and fructose; and xymase, another yeast enzyme, causes the conversion of glucose, but not of the analogous compound fructose, into ethyl alcohol and carbon dioxide.

72. Water as a Catalyzer.—The presence of water in at least minute quantity is essential to the occurrence of almost all reactions. This is shown by experiments upon some of the most energetic chemical changes, such as the combination of sodium with chlorine, the union of ammonia and hydrogen chloride gases, the combustion of carbon monoxide with oxygen, and the union of lime and sulphur trioxide, which are found not to take place when the separate substances are very thoroughly dried before they are brought together.

THE EFFECT OF TEMPERATURE

73. The Law of Temperature-Effect.—Equal small increments of temperature cause an approximately equal multiplication of the specific rate of any definite reaction. Thus, if the specific rate of a reaction is increased 2.5-fold by raising the temperature from 0 to 10°, it will again be increased approximately 2.5-fold by raising the temperature from 10 to 20°.

The deviations from this law are greater, the greater the interval of temperature to which it is applied. The general magnitude of them is illustrated by the ratios of the specific reaction-rates at 10° intervals for the third-order reaction between ferrous chloride, potassium chlorate, and hydrochloric acid, which have been found to be

as follows: 2.8 between 0 and 10°, 2.7 between 10 and 20°, 2.4 between 20 and 30°, 2.5 between 30 and 40°, and 2.2 between 40 and 50°.

Prob. 19. In a solution 0.01 molal in sodium hydroxide and 0.01 molal in ethyl acetate, 39% of the ethyl acetate is decomposed in 10 minutes at 25°, and 55% at 35°. How long would it take to decompose 55% at 15°?

Prob. 20. A more general expression of the law of temperature-effect is that given by the equation $d \log k = (A/T^2) dT$, in which A is a quantity which has nearly the same value at temperatures not far apart. Integrate this equation, and show that the result for a small range of temperature is in accordance with the above stated law of temperature-effect.

Prob. 21. Calculate by this more general expression from the data of Prob. 19 how long it would take to decompose 50% of the ethyl acetate at 20°.

With respect to the effect of temperature, it is further to be noted that in the case of different reactions equal small increments of temperature cause not far from the same multiplication of their specific rates. Thus, a 10° rise of temperature multiplies the specific rates of the reactions between the following substances by the following factors:

$$NaOH + C_2H_5C_2H_3O_2 \text{ (at } 27°\text{)}: \quad 1.9$$
$$FeSO_4 + KClO_3 + H_2SO_4 \text{ (at } 21°\text{)}: \quad 2.4$$
$$NaOH + CH_2ClCO_2Na \text{ (at } 100°\text{)}: \quad 2.5$$
$$C_{12}H_{22}O_{11} + H_2O \text{ (+ HCl) (at } 40°\text{)}: \quad 3.6$$

Prob. 22. At 100° a certain reaction takes place to an extent of 25% in one hour. Estimate roughly how long it would take for the reaction to proceed to the same extent at 20°.

THE EFFECT OF SURFACE IN THE CASE OF SOLID SUBSTANCES

74. Solid Substances Involved in Chemical Reactions.—When a solid substance is reacting with a solute, the quantity of it dissolved per unit of time is proportional to the surface of the solid, as well as to the concentration of the solute that reacts with it. Thus, when a dilute solution of acetic acid in contact with a compact mass of magnesium oxide is uniformly stirred, the quantity of the oxide dissolved is proportional to the surface of the mass and to the concentration of the acetic acid.

In reactions with solid substances, it is to be borne in mind that, owing to corrosion, the effective surface is constantly changing, and that the concentration of the solution in contact with the solid is the same as that of the whole solution only when there is adequate stirring.

75. Solid Substances Dissolving in Their Own Solutions.—When a solid substance is dissolving at a definite temperature in its own (partially saturated) solution, the quantity dissolved per unit of time is proportional to the surface of the solid and to the difference between the concentration of the saturated solution and that of the solution in contact with the solid.

Prob. 23. A quantity of a solid substance having a surface-area a and a solubility s is stirred uniformly at a definite temperature with a definite volume v of water. *a.* Formulate a differential expression for the rate at which the concentration c of the solution will increase. *b.* Integrate this expression, assuming the surface to remain constant (which it does approximately when the quantity of the solid substance is very large in relation to the quantity of it that dissolves).

Prob. 24. a. What are the relative rates at which a substance dissolves in its own solution when the solution is 50% and 95% saturated, assuming the surface of the solid and the volume of the solution to be the same in the two cases? *b.* If it takes 2 minutes for the solution to become 50% saturated, how long will it take for the degree of saturation to increase from 95 to 98%?

SIMULTANEOUS REACTIONS

76. Law of Independent Reaction-Rates.—When two reactions are taking place simultaneously, the rate of each is determined by its own specific reaction-rate and by the concentrations of the substances involved in it, just as if the other reaction were not taking place.

Prob. 25. The reaction between methyl oxalate and sodium hydroxide takes place in the two stages:

$$(CH_3)_2C_2O_4 + NaOH = CH_3NaC_2O_4 + CH_3OH$$
$$CH_3NaC_2O_4 + NaOH = Na_2C_2O_4 + CH_3OH.$$
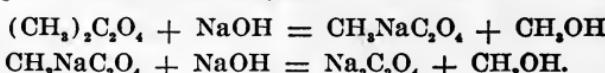
Formulate the differential equation for the rate (expressed in molal concentration) of each of these reactions for the case that the methyl oxalate and sodium hydroxide are present at the start at the molal concentrations c_A and c_B, respectively, and that at the time t the sodium methyl oxalate and the sodium oxalate produced have attained the molal concentrations c_1 and c_2, respectively.

77. Reactions Taking Place in Opposite Directions.—The law of independent reaction-rates finds an especially important application in the case of reactions which do not go to completion, but take place in one direction when the substances on the one side of the chemical equation are brought together, and in the other direction when those on the other side are brought together. The resultant rate of such a reaction must evidently be the difference of the rates of the two opposing reactions.

Prob. 26. The gaseous reaction $H_2 + I_2 = 2HI$ is an incomplete reaction of the kind just described, which at 400–500° takes place at a measurable rate. For the case that hydrogen, iodine, and hydrogen iodide are present at the start at the molal concentrations c_{0H}, c_{0I}, and c_{0HI}, formulate the differential expression for the rate at which the molal concentration of the hydrogen iodide is increasing at the time t, when c mols per liter of hydrogen iodide have been produced.

CHAPTER VI

THE EQUILIBRIUM AT CONSTANT TEMPERATURE OF CHEMICAL REACTIONS INVOLVING GASEOUS OR DISSOLVED SUBSTANCES AT SMALL CONCENTRATIONS

THE LAW OF MASS–ACTION

78. The Equilibrium of Chemical Reactions.—When two or more chemical substances capable of reacting with one another are brought together, it is always true after a sufficiently long time (which may vary from a fraction of a second to thousands of years) that the chemical reaction which has been taking place between them practically ceases—in other words, that a condition is reached where no further change takes place. The reaction is then said to be in *equilibrium*.

Many reactions (for example, the reaction $NH_4OH + HBO_2 = NH_4BO_2 + H_2O$ in aqueous solution) take place so incompletely that at equilibrium the substances on both sides of the equation are present in measurable proportions. But with many other reactions the equilibrium-conditions are such that the change seems to take place completely when the substances on one side of the chemical equation expressing it are brought together, and not to take place at all when the substances on the other side are brought together; thus, this is true of the reaction $NaOH + HCl = NaCl + H_2O$ in aqueous solution. In all such cases, however, the gaseous or dissolved substances on both sides of the equation are really present at some concentration, though this may be so small in the case of some of the substances that it cannot be directly measured.

Reactions (like that in a mixture of hydrogen and oxygen at 25°) which are taking place so slowly that no appreciable change can be detected within a reasonable time are not to be confounded with those which are in a state of equilibrium. Whether equilibrium-conditions have been attained can be determined by causing the reaction to take place in the two opposite directions and comparing

the concentrations of the substances in the two cases after equilibrium seems to have been reached.

The equilibrium-conditions of chemical reactions vary with the temperature. In this chapter and the following one the principles will be discussed which determine equilibrium when the temperature has any constant value.

79. The Mass-Action Law.—The effect of concentration in determining chemical equilibrium is expressed by one of the most fundamental laws of chemistry. This law, which is commonly known as the *mass-action law,* states that, whatever be the initial concentrations of the gaseous or dissolved substances A, B, . . E, F, . . involved in any definite chemical reaction, such as may be represented in general by the equation, $aA + bB.. = eE + fF..$, the reaction always takes place in such a direction and to such an extent that, when equilibrium is reached at any definite temperature, the conditions are satisfied which are expressed by the equation:

$$\frac{c_E{}^e\, c_F{}^f \cdots}{c_A{}^a\, c_B{}^b \cdots} = K, \text{ a constant.}$$

In this expression c_E, c_F, . . c_A, c_B, . . denote the concentrations of the substances E, F,.. A, B,.. in the equilibrium mixture, and $e, f,.. a, b,..$ denote the number of mols of them that are involved in the reaction expressed by the chemical equation.

The quantity K, which is a constant characteristic of the reaction, is called its *equilibrium-constant.* Its value is, of course, constant with respect to variations of the initial and equilibrium concentrations, but it varies with the temperature. In evaluating it, it is customary to express all concentrations in mols per liter, and to place in the numerator the concentrations of the substances occurring on the right-hand side of the chemical equation written in some specified way. In which direction the chemical equation is written is, of course, arbitrary in the case of reactions at equilibrium. With many types of reactions, however, it is more natural to write the equation in one of the two directions; and in such cases the usage in evaluating the equilibrium-constant has become fairly definite. This usage will be illustrated by the examples given in the following articles.

The mass-action law has been verified by direct experiments upon a large number of different reactions. It can be derived, as will be

shown in a later chapter, with the aid of the laws of thermodynamics, from the perfect-gas equation $(p = c\,R\,T)$, or from the osmotic-pressure equation for perfect solutes $(P = c\,R\,T)$. It can be also derived from the laws of the rate of reactions, as is illustrated by Prob. 1 below.

The mass-action law is exact only in the case of reactions between perfect gases or perfect solutes; but it holds true approximately when applied to gases at moderate pressures or to unionized or slightly ionized solutes at moderate concentrations. The deviations from it in such cases may be expected to be of the same order of magnitude as those from the pressure-concentration law of perfect gases or perfect solutes. As will be seen later, large deviations are met with in the case of largely ionized substances.

Prob. 1. a. Formulate the mass-action expression for the equilibrium of the reaction $2HI = H_2 + I_2$, and derive it from the differential equation obtained in Prob. 26 of the previous chapter, explaining the substitutions that are made in the derivation. *b.* Show what relation exists between the equilibrium-constant and the specific reaction-rates.

Note.—Although the law of chemical equilibrium can be derived, as here illustrated, from the law of reaction-rate, an important difference between the two laws is to be noted. Namely, it can be shown that, although the expression for the rate of a reaction depends on its mechanism, the same expression is obtained for its equilibrium, whatever be the process by which it is considered to be attained. In using the equilibrium expression it is only necessary to know the concentrations of the substances actually occurring in that expression.

APPLICATIONS OF THE MASS–ACTION LAW TO GASEOUS SUBSTANCES

80. Expression of the Law in Terms of Partial Pressures.—In applications of the mass-action law to gases, it is usual to substitute for the concentrations of the substances in the equilibrium-mixture their partial pressures. This is admissible since at any definite temperature the two quantities are proportional to one another, in virtue of the relation $p = c\,R\,T$.

The general mass-action expression in terms of partial pressures evidently is

$$\frac{p_E{}^e\,p_F{}^f\cdots}{p_A{}^a\,p_B{}^b\cdots} = K_p,$$

where K_p is a constant, called the equilibrium-constant in terms of

pressure, which has in general a different numerical value from the constant K occurring in the corresponding concentration-expression. In evaluating it the partial pressures are commonly expressed in atmospheres.

Prob. 2. Derive the general mass-action expression in terms of pressure from that in terms of concentration, and show the relation between the two equilibrium-constants.

81. Gaseous Dissociation.—A chemical change which consists in the splitting of a substance with complex molecules into one or more substances with simpler molecules is called dissociation. Thus, the reactions $I_2 = 2I$, $NH_4Cl = NH_3 + HCl$, and $2CO_2 = 2CO + O_2$, are examples of dissociation. The fractional extent to which the dissociating substance has been decomposed is called its degree of dissociation, or simply its *dissociation* (γ). The equilibrium-constant of such a reaction is commonly called the *dissociation-constant* of the dissociating substance.

It is characteristic of such reactions that the number of molecules increases when the dissociation increases. Since the pressure-volume product of gases increases correspondingly, the degree of dissociation can always be determined by measuring the volume or density of the gas at a known temperature and pressure, and comparing it with that calculated for the undissociated or completely dissociated substance, as is illustrated by Prob. 14, Art. 17, and by Prob. 4 below.

Another common method of determining the composition of the equilibrium-mixture is to cool it suddenly to a lower temperature at which the reaction-rate is so small that the original equilibrium is not displaced, and then to analyze the mixture. This method presupposes that there is no change in the composition during the short period of cooling. This condition may be practically realized in cases where the rate at which the equilibrium is established is comparatively slow even at the higher temperature, or in cases where the reaction takes place only in contact with a catalyzer. In the latter case the equilibrium-mixture can be separated from the catalyzer, and subsequently cooled without the danger of any change taking place.

Prob. 3. a. Formulate the mass-action expression for the dissociation of sulphur trioxide into sulphur dioxide and oxygen. *b.* At 630°

and 1 atm. the sulphur trioxide is just one third dissociated. Calculate the dissociation-constant of sulphur trioxide.

Prob. 4. Show how the dissociation (γ) of sulphur trioxide could be calculated from measurements of the density (d) of the equilibrium mixture at the temperature (T) and pressure (p) in question.

Prob. 5. A mixture consisting of 1 mol of SO_2 and 1 mol of O_2 is passed at 630° and 1 atm. through a tube containing finely divided platinum so slowly that equilibrium is attained, and the issuing gas is cooled and analyzed by absorbing the sulphur dioxide and trioxide by potassium hydroxide and measuring the residual oxygen gas. At 0° and 1 atm. the volume of this residual gas was found to be 13,780 cc., corresponding to 0.615 mol. *a.* Calculate the dissociation-constant of sulphur trioxide. *b.* Calculate the ratio of the mols of sulphur trioxide to the mols of sulphur dioxide in an equilibrium mixture at 630° in which the partial pressure of oxygen is 0.25 atm.

Prob. 6. At a certain temperature a definite quantity of phosphorus pentachloride gas has at 1 atm. a volume of 1 liter, and under these conditions it is about 50% dissociated into PCl_3 and Cl_2. Show by reference to the mass-action expression whether the dissociation will be increased or decreased: *a*, when the pressure on the gas is reduced till the volume becomes 2 l.; *b*, when nitrogen is mixed with the gas till the volume becomes 2 l., the pressure being still 1 atm.; *c*, when nitrogen is mixed with the gas till the pressure becomes 2 atm., the volume being still 1 l.; *d*, when chlorine is mixed with the gas till the pressure becomes 2 atm., the volume being still 1 l.—In answering these questions consider whether the first effect of the change in conditions (assuming that no reaction takes place) is to increase or decrease the value of the ratio $p_{Cl_2} p_{PCl_3}/p_{PCl_5}$, and in which direction the reaction must take place in order to restore the equilibrium-value of this ratio.

Prob. 7. a. Derive for the dissociation of water-vapor into hydrogen and oxygen a mass-action expression which will show how the dissociation (γ) varies with the total pressure (p). *b.* At 2,000° the dissociation is 2.0% when the total pressure is 1 atm. How much is the dissociation when the total pressure is 0.2 atm. (as it is approximately in the gaseous mixture produced by burning hydrogen with the minimum amount of air)? Solve the equation approximately, neglecting the (small) value of the dissociation where this is justifiable.

82. Metathetical Gas Reactions.

—Examples of such reactions whose equilibrium has been investigated are: $2HI = H_2 + I_2^*$; $CO_2 + H_2 = CO + H_2O$; and $4HCl + O_2 = 2Cl_2 + 2H_2O$.

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*This reaction is often called a dissociation, since one substance is converted into two others. From a molecular standpoint, however, it consists in an interchange of atoms between molecules, rather than in a splitting of a molecule into simpler ones; and from a mass-action standpoint it differs from true dissociation in that there is no increase in the number of molecules when the reaction takes place.

An important principle in regard to them, illustrated by Prob. 9 below, is that the equilibrium-constant of any metathetical gas reaction can be calculated from the dissociation-constants of the compounds involved in it.

Another important principle relates to the effect of pressure. It states that increase of pressure causes the equilibrium of any gaseous reaction to be displaced in that direction in which the number of molecules, and therefore the volume of the gas, decreases. This principle has already been illustrated by the fact that dissociation is decreased by increase of pressure. It is demonstrated by Prob. 10.

Prob. 8. The equilibrium-constant of the reaction $CO_2 + H_2 = CO + H_2O$ at 1,120° is 2.0. What is the ratio of the number of mols of CO_2 and of H_2O that will be formed when a "water-gas" consisting of 1 mol CO and 1 mol H_2 is burnt at 1,120° with $\frac{1}{2}$ mol O_2? (Assume that equilibrium is attained and that the quantity of the oxygen which remains uncombined is negligible.)

Prob. 9. The equilibrium-constant of the reaction $2CO_2 = 2CO + O_2$ at 1,120° is 1.4×10^{-12}. *a.* Calculate the partial pressure of the oxygen in the equilibrium mixture of Prob. 8. *b.* Calculate the dissociation-constant of water-vapor at 1,120°. *c.* Show what relation exists between the dissociation-constants K_W and K_{CO_2} of water-vapor and of carbon dioxide and the equilibrium-constant K of the reaction $CO_2 + H_2 = CO + H_2O$.

Prob. 10. Prove that the equilibrium of any chemical reaction, $aA + bB = eE + fF$, must be displaced in the direction in which the number of molecules decreases when the total pressure p of the equilibrium mixture (in which the substances are present at mol-fractions x_A, x_B, x_E, and x_F) is increased.

APPLICATIONS OF THE MASS–ACTION LAW TO DISSOLVED SUBSTANCES

83. Ionization or Slightly Ionized Univalent Acids and Bases.— The mass-action law has been found to be applicable to the ionization (dissociation into ions) of the slightly ionized monobasic acids and monacidic bases. This is illustrated by the following values of the percentage ionization at 18° derived from conductance measurements (as described in Art. 55) and of the ionization-constant K of ammonium hydroxide (that is, the equilibrium-constant of the reaction $NH_4OH = NH_4^+ + OH^-$):

Conc.	0.300	0.100	0.010	0.001
$100\,\gamma$	0.74	1.30	4.05	12.3
$10^6 K$	16.6	17.1	17.1	17.1

The ionization-constant varies greatly with the composition and structure of the acid or base, as will be seen from the following values of it for certain acids at 25°.

Acid	10^6K	*Acid*	10^6K	*Acid*	*Values of 10^6K*		
HCN	0.0007	HCO_2H	210.	$C_6H_5CO_2H$	60.	60.	60.
HBO_2	0.0007	CH_3CO_2H	18.		*Ortho*	*Meta*	*Para*
HClO	0.04	$C_2H_5CO_2H$	13.	$C_6H_4OHCO_2H$	1020.	87.	29.
HNO_2	500.	$n\text{-}C_3H_7CO_2H$	15.	$C_6H_4ClCO_2H$	1320.	155.	93.
				$C_6H_4NO_2CO_2H$	6160.	345.	396.

Prob. 11. At 25° acetic acid in 0.1 normal solution is 1.34% ionized. *a.* Calculate the ionization-constant of acetic acid. *b.* Calculate its ionization in 0.01 normal solution.

Prob. 12.—Effect of the Presence of a Substance with a Common Ion.—a. Show that the hydrogen-ion concentration in an acetic acid solution is decreased by the addition of sodium acetate approximately in the proportion in which the concentration of the acetate-ion is increased. *b.* State the corresponding principle that would apply to the ionization of ammonium hydroxide in the presence of an ammonium salt. *c.* Calculate the ionization of acetic acid in a solution 0.1 normal both in acetic acid and in sodium acetate, the sodium acetate in the mixture being 85% ionized.—In this and other mass-action problems make any simplifications that will not produce in the result an error greater than 1%.

84. Ionization of Dibasic Acids and Their Acid Salts.—Polybasic acids ionize in stages; thus, a bibasic acid H_2A ionizes according to the equations $H_2A = H^+ + HA^-$ and $HA^- = H^+ + A^=$. The equilibrium-constants K_1 and K_2 of these reactions are called the ionization-constants for the first hydrogen and for the second hydrogen, respectively. The values of K_2 are commonly much smaller than those of K_1. The values at 25° of the two constants for some important acids are as follows:

Acid	K_1	K_2
H_2SO_3	2×10^{-2}	5×10^{-6}
H_3PO_4	1×10^{-2}	2×10^{-7}
$H_2C_4H_4O_6$ (tartaric)	9.7×10^{-4}	4×10^{-5}
H_2CO_3	3×10^{-7}	3×10^{-11}
H_2S	9×10^{-8}	1×10^{-15}

From the two ionization-constants of a dibasic acid and its formal concentration c the concentrations of the various substances H_2A, HA^-, $A^=$, and H^+ present in its solution can be calculated. In solving any such mass-action problem, the best plan is to formulate firs⁺

the equilibrium equations that must be satisfied—thus, in this case the equations $(H^+)(HA^-) = K_1(H_2A)$ and $(H^+)(A^=) = K_2(HA^-)$.* The next step is to formulate the so-called condition equations, which sum up the concentrations of the separate forms in which an element or other constituent exists in the solution. Thus, in this case, for the total molal concentration $\Sigma(A)$ of the constituent A, and for that $\Sigma(H)$ of the hydrogen, we have:

$$(H_2A) + (HA^-) + (A^=) = \Sigma(A) = c,$$
$$\text{and } (H^+) + (HA^-) + 2(H_2A) = \Sigma(H) = 2c.$$

(It will be noted that one of these equations might be replaced by a simpler condition-equation of another kind; namely, by the equation, $(H^+) = (HA^-) + 2(A^=)$, which expresses the fact that positive and negative ions must be present in equivalent quantities.) We now have four independent equations containing four unknown concentrations. An exact algebraic solution of these equations is therefore possible. But, as such a solution is often very complicated, it is advisable to try first to simplify the condition-equations, which can often be done by neglecting in them the concentration of some substance which is small in comparison with the concentrations of the other substances. Thus, in this case the concentration $(A^=)$ is small compared with the concentration (HA^-), for the reasons that K_2 is small in comparison with K_1 and that the hydrogen-ion produced by the ionization of the H_2A into H^+ and HA^- further decreases by the common-ion effect the ionization of the HA^-. It is always well to test the correctness of such simplifying assumptions by subsequent calculation of the quantity neglected.

Prob. 13. From the ionization-constants given in the table above, calculate by the method just described the molal concentration of each of the substances present in a 0.01 formal solution of tartaric acid at 25°.

Prob. 14.—Determination of the Ionization-Constant for the Second Hydrogen by Reaction-Rate Measurements.—By measuring the conductance of tartaric acid in 0.06–0.01 formal solution, where the ionization of the second hydrogen is negligible, the ionization-constant for the first hydrogen of the acid has been found to be 0.00097 at 25°. The hydrogen-ion concentration in a 0.1 formal solution of sodium hydrogen tartrate, NaHA, was found in Prob. 18, Art. 70, to be 0.0002 molal. From analogy with other salts of the same type (see Art. 58) the

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*As is done here, the molal concentrations of substances are often represented by writing their formulas within parentheses.

concentration (NaHA) of unionized sodium hydrogen tartrate in this solution may be estimated to be 0.016 molal. In regard to the concentrations (Na_2A) and (NaA⁻) nothing definite is known, but they may be assumed in this problem to be negligibly small. From these data calculate the concentrations (A⁼), (HA⁻), and (H_2A), and the ionization-constant for the second hydrogen of tartaric acid. (In this case no simplification of the condition-equations is admissible, other than the neglecting of the concentrations (Na_2A) and (NaA⁻) just mentioned.) Tabulate the molal concentrations of all the substances present in the solution of the sodium hydrogen tartrate.

Prob. 15.—Determination of the Ionization-Constant for the Second Hydrogen by Distribution Experiments.—A 0.1 formal solution of sodium hydrogen succinate NaHA in water is found by experiment to be in equilibrium at 25° with a 0.00187 formal solution of succinic acid in ether. The distribution-ratio of succinic acid between water and ether at 25° is 7.5. *a.* Find the H_2A concentration in the aqueous solution of the acid salt. *b.* Calculate the ionization-constant for the second hydrogen. That for the first hydrogen is 6.6×10^{-5}. Make the same assumptions as in Prob. 14; neglect also the value of (H⁺) in the condition-equation, and show afterwards by calculating it that it was justifiable to neglect it.

85. The Ionization of Water.

Prob. 16. Show that the product (H⁺) × (OH⁻) has substantially the same value in any dilute aqueous solution (up to 0.1–0.2 normal) as in pure water. (This constant value of the (H⁺) × (OH⁻) product is called the ionization-constant K_W of water.)

Note.—The application, involved in this problem, of the mass-action law to a constituent so concentrated as the solvent would seem to be inadmissible, and is so in a strict sense. It can be shown, however, with the aid of thermodynamics, that the activity of the solvent, that is, its mass-action effect in influencing equilibrium, is exactly proportional in the case of different solutions to the vapor-pressure of the solvent above those solutions. And it follows from Raoult's law of vapor-pressure that the vapor-pressure of even a 0.5 molal aqueous solution is only about 1% less than that of pure water.

Prob. 17. At 25° the concentration of hydroxide-ion in pure water is one tenmillionth molal. What is its concentration in 0.1 formal HCl solution, in which the acid is 92% ionized?

86. Ionization of Largely Ionized Substances.—In the case of salts and of largely ionized acids and bases the ionization values derived from conductance or from freezing-point measurements do not change with the concentration even approximately in accordance with the mass-action law. Thus, the average ionization values (γ obs.) for uni-univalent salts given in Art. 58, the "ionization-constants" (K)

calculated from them, and the ionization values (γ calc.) calculated conversely from the value of this constant at 0.1 normal are as follows:

Conc.	0.001	0.01	0.02	0.05	0.10
γ obs.	0.96	0.92	0.90	0.87	0.84
γ calc.	0.998	0.98	0.96	0.91	0.84
K	0.023	0.11	0.16	0.29	0.44
$K/\sqrt{c}$	(0.73)	1.10	1.13	1.30	1.39

It has been found empirically that the "ionization-constant" K varies with the concentration c of the salt, and is approximately proportional to the square-root of that concentration. This is illustrated by the comparatively small variations of the values of $K/\sqrt{c}$ given in the last row of the above table. This principle applies also to mixtures of salts, the "ionization-constant" being in this case dependent on the sum of the concentrations (Σc) of all the salts in the mixture. Thus, for a salt A^+B^- the principle is expressed by the equation:

$$\frac{(A^+) \times (B^-)}{(AB)} = K = \text{const.} \times \sqrt{\Sigma c}.$$

Prob. 18. a. Show that this principle requires that in a mixture of two uniunivalent salts with a common-ion (such as K^+Cl^- and Na^+Cl^-) the ionizations of the two salts are equal, whatever be the relative proportions of the two salts in the mixture. *b.* Show that the principle further requires that the ionization γ_1 or γ_2 of either salt in the mixture is equal to the ionization γ which it has when it alone is present at a concentration c equal to the sum of the concentrations ($c_1 + c_2$) of the two salts.

Prob. 19. What are the concentrations of unionized potassium chloride and of unionized sodium chloride in a mixture 0.02 normal in KCl and 0.08 normal in NaCl?

The reason why largely ionized substances do not conform to the mass-action law is not known. One possible explanation of this anomaly is that the mass-action law really holds true in the case of largely ionized substances, but that the conductance-ratio is not an exact measure of their ionization. This would imply that the mobility of the ions does not remain constant even up to moderate concentrations, as was assumed in Art. 55. Another explanation is that the activity either of the ions or of the unionized substance or of both is abnormal—in other words, that the mass-action effect is not proportional to the concentration.

The simplest way of accounting fairly satisfactorily for the

behavior of largely ionized substances in all their relations seems at the present time to be the adoption of the following hypotheses: (1) the conductance-ratio is a substantially correct measure of their ionization; (2) the ions have (approximately) normal activities; and (3) the unionized substance has an activity which is far from being proportional to its concentration. These assumptions will therefore be employed in this book. And in accordance with them, in dealing with mass-action problems, the equilibrium-equations will always be so written as to involve the ions rather than the unionized part of largely ionized substances; and in condition-equations the concentrations of the unionized parts of such substances will be calculated, not from their ionization-constants, but from the ionization-values which are obtained from the conductance-ratio or from the average values for salts of the same valence type.

Prob. 20. Formulate the equilibrium equation for each of the following reactions (taking place in dilute aqueous solution) :

$Cl_2 + H_2O = HCl + HClO$; and $Cl_2 + H_2O = H^+ + Cl^- + HClO$. Show that both of these equilibrium equations cannot hold true, since the mass-action law does not apply to the simple ionization of largely ionized acids.

Prob. 21. When a 0.06 molal solution of Cl_2 is allowed to stand at 0° till equilibrium is reached, 31% of the chlorine is converted into hypochlorous acid and hydrochloric acid. *a.* Calculate the equilibrium-constant of the reaction, assuming that the ionization of hydrochloric acid is 95%. *b.* Calculate what the initial concentration of the chlorine must be in order that 50% of it may be converted into hypochlorous and hydrochloric acids in the equilibrium mixture.

87. The Hydrolysis of Salts.—When either the acid or base of a salt has a very small ionization-constant, the salt in aqueous solution reacts with the water to an appreciable extent with formation of the acid and base. Thus, potassium cyanide in 0.01 normal solution at 25° is decomposed to an extent of 3.5% according to the reaction $K^+CN^- + H_2O = K^+OH^- + HCN$.* This phenomenon is called hydrolysis; and the fraction of the salt hydrolyzed is called the degree of hydrolysis, or simply the *hydrolysis* (*h*). The equilibrium-constant of a hydrolytic reaction is called the *hydrolysis-constant* of the salt.

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*As is done in this case, it is convenient to indicate largely ionized substances, whose ionization does not conform to the mass-action law, by attaching + and — signs to their ions, and to omit such signs in the case of slightly ionized substances, whose ionization conforms to that law.

Prob. 22. a. Derive a mass-action expression showing how the hydrolysis of a salt like potassium cyanide varies with the concentration of the salt. *b.* From the data given in the preceding text calculate the degree of hydrolysis and the concentration of free base in a 0.1 normal KCN solution at 25°.—Assume that the ionizations of the salt and free base are equal.

Prob. 23. Derive a mass-action expression showing how the hydrolysis of a salt like ammonium cyanide, of which the acid and base are both slightly ionized, varies with the concentration and ionization of the salt.

Prob. 24. In 0.1 formal solution at 25° ammonium cyanide is 40% hydrolyzed. What is its hydrolysis in 0.01 formal solution? For the ionization values refer to Art. 86.

Prob. 25. Show how the hydrolysis-constants of salts like potassium cyanide and ammonium cyanide are related to the ionization-constants of water (K_W), of the acid (K_A), and of the base (K_B).

Prob. 26. Calculate the hydrolysis of ammonium acetate in 0.1 formal solution at 25° from the ionization-constants involved. (The ionization-constants of acetic acid and of ammonium hydroxide have the same value (1.8×10^{-5}) at 25°.)

Prob. 27. At 100° the ionization-constant of water is 50×10^{-14}; that of acetic acid is 1.1×10^{-5}; and that of ammonium hydroxide is 1.4×10^{-5}. Calculate the hydrolysis of ammonium acetate in 0.1 formal solution at 100°, and compare it with that at 25°. Assume the ionization of the salt to be the same as at 25°.

Prob. 28.—Determination of Hydrolysis by Distribution Experiments.—A 0.05 formal solution of $Na_2NH_4PO_4$ in water is found to be in equilibrium with a 0.00173 formal solution of NH_3 in chloroform at 18°. What is the hydrolysis of the salt? The distribution-ratio for NH_3 between water and chloroform at 18° is 27.5.

Prob. 29.—Determination of Hydrolysis by Reaction-Rate Experiments.—The specific reaction-rate at 100° of the sugar hydrolysis has been found to be 0.0386 in a solution 0.001 normal in HCl, and to be 0.0946 in a solution 0.01 formal in $AlCl_3$. What fraction of the salt is hydrolyzed (into $Al(OH)_3$ and 3HCl)?

Prob. 30.—Determination of Hydrolysis by Conductance Measurements.—The specific conductance at 100° of a 0.025 formal solution of NH_4Ac (ammonium acetate) is 0.00685 reciprocal ohms; and that of a solution 0.025 formal in NH_4Ac and 0.025 formal in NH_4OH is 0.00717 reciprocal ohms. *a.* Calculate the hydrolysis of the ammonium acetate in the first solution, assuming that in the second solution the hydrolysis of the salt and the conductance of the base are both negligible. *b.* Calculate the hydrolysis of the salt in the second solution. *c.* Calculate the specific conductance of the free base in the second solution. The Λ_0-value for NH_4OH at 100° is 647.

88. Displacement of One Acid or Base from its Salt by Another.— One of the most important types of equilibrium in aqueous solution is the partial displacement of one acid or base from its salt by another; for example, that of acetic acid from sodium acetate by formic acid, or that of ammonium hydroxide from ammonium chloride by sodium hydroxide. This phenomenon has been studied experimentally by the methods illustrated by Probs. 35–37. Before the mass-action relations involved were fully understood, the extent of the displacement was taken as a measure of the relative strengths of different acids or bases; those which are largely displaced from their salts being called weak acids or bases, and those which cause such displacement being called strong acids or bases. It is shown by Probs. 31–33 that the mass-action law and ionic theory give a comparatively simple explanation of this phenomenon in the case of not largely ionized univalent acids or bases; also that the relative strengths of different acids or bases are determined by their ionization, weak ones being those which are slightly ionized and strong ones those which are largely ionized.

Prob. 31. To a 0.1 normal solution of KNO_2 is added at 25° an equal volume of a 0.1 normal solution of acetic acid. *a.* Calculate the fraction of the potassium nitrite that is converted into potassium acetate. *b.* Calculate the fraction that would be so converted if the acetic acid solution were 1.0 normal (instead of 0.1 normal).

Prob. 32. *a.* For the general case expressed by the equation $B^+A^- + HA' = B^+A'^- + HA$ where the solution is originally c-formal in B^+A^- and c'-formal in HA', derive an expression for the fraction x of the salt B^+A^- converted into the salt $B^+A'^-$, assuming that the acids are not largely ionized. *b.* Derive from this expression the relation between the ionization-constants of the acids and the fractions of the basic constituent that are combined with the two acidic constituents for the case that $c = c'$; and state the principle fully in words.

Prob. 33. To a liter of 0.1 normal HCl is added at 25° a liter of 0.1 normal ammonia ($K = 0.000018$) and a liter of 0.1 normal methylamine ($K = 0.00050$). Calculate the fraction of the acid which combines with each base.

Prob. 34. A 0.1 formal solution of acetic acid is added to an equal volume of 0.1 formal $NaHCO_3$ solution at 25°, the carbon dioxide produced being kept above the solution at a pressure of 1 atm. Calculate the concentrations of the two salts and two acids in the resulting solution (looking up the data needed). Compare this result with that calculated for the case where no carbon dioxide is allowed to escape from the solution.

Prob. 35.—Determination of Displacement by Volume Measurements.—When 1000 g. of a solution containing 1KOH is mixed with 1000 g. of a solution containing $1CH_3CO_2H$ there is an increase of volume of 9.52 ccm. When the former solution is mixed with 1000 g. of a solution containing $1HCO_2H$ there is an increase of volume of 12.39 ccm. When 2000 g. of a solution containing $1HCO_2K$ is mixed with 1000 g. of one containing $1CH_3CO_2H$ there is a decrease of volume of 0.74 ccm. Determine what fraction of the formic acid is displaced from its salt by the acetic acid. Compare this result with that calculated from the ionization-constants.

Note.—The displacement may also be determined experimentally by measuring the quantities of heat evolved, instead of the changes of volume, when solutions are mixed as in the preceding problem.

Prob. 36.—Determination of Displacement by Color Measurements.—Paranitrophenol is a slightly ionized acid whose solution is colorless, while solutions of its salts have a yellow color which increases proportionately with the quantity of salt. 25 ccm. of a 0.01 normal solution of paranitrophenol are placed in each of two tubes of the same diameter; to one tube are added 25 ccm. of a 0.01 normal solution of potassium acetate; and to the other tube is added 0.01 normal KOH solution until on looking down through the tubes the colors are seen to be the same, 1.65 ccm. of the KOH solution being required. Calculate the fraction of the paranitrophenol which exists in the first mixture in the form of its salt; and calculate the ionization-constant of the paranitrophenol.

Prob. 37. Suggest a method (different from those already mentioned) by which the displacement of ammonium hydroxide from ammonium chloride by sodium hydroxide might be determined.

89. Neutralization-Indicators.—An acid neutralization-indicator (such as litmus, paranitrophenol, or phenol phthalein) is a mixture of two isomeric acids* (HIn' and HIn'') in equilibrium with each other, one of which (HIn'') is present in much smaller proportion but is so much more ionized than the other (HIn') that when a base BOH is added the salt produced is almost wholly of the form $B^+In''^-$. The substances HIn' and $B^+In'^-$ are different in color from the substances HIn'' and $B^+In''^-$, the color being determined only by the molecular structure of the group In. It follows from these conditions that the

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*Thus the formulas commonly assigned to phenol phthalein and its potassium salt are:

$$C_6H_4 - C \underset{CO\ -\ O}{\overset{/C_6H_4OH}{\diagdown C_6H_4OH}} \quad \text{and} \quad C_6H_4 - C \underset{COOK}{\overset{/C_6H_4OK}{\diagdown C_6H_4 = O}}.$$
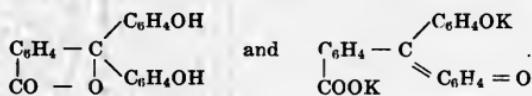
indicator acid changes color when converted into its salt. It will also be evident from Prob. 38 that the indicator behaves as if it were a single acid HIn whose salt has a different color from the acid itself.

Prob. 38. Show by formulating the equilibrium equation that in the case of an indicator such as has been described $\dfrac{(H^+)(In'')}{(HIn')} = \text{const.}$

Note.—This constant, which is a product of two equilibrium-constants, will be called the indicator-constant K_I.

Prob. 39. Derive a relation between the hydrogen-ion concentration (H^+), the indicator-constant K_I, and the fraction x of the indicator which is converted into the colored form existing in alkaline solution. (This fraction will hereafter be called simply the fraction of the indicator transformed.)—In indicator problems the ionization of the indicator salt, as well as that of any other salt present, may be regarded as complete, since only approximate results are ordinarily desired.

The relations in the case of basic indicators (existing almost wholly in the two differently colored forms In'OH and In'''$^+$A$^-$) are entirely similar to those in the case of acid indicators. By formulating the mass-action equations, it can, in fact, be shown that the relation derived in Prob. 39 between the hydrogen-ion concentration and the fraction (x) of the indicator transformed holds true also in the case of basic indicators. By adopting as the value of the indicator-constant that calculated by the equation $K_I = \dfrac{x\,(H^+)}{1-x}$ a basic indicator may therefore be treated as an acid indicator; and it will be so treated in the following problems.

Prob. 40.—Determination of the Indicator-Constant.—To 100 ccm. of a solution 0.1 normal in K^+Ac^- and 0.01 normal in HAc are added 10 ccm. of a 0.01 normal solution of paranitrophenol. This solution is found to have the same color as a solution made by adding 0.50 ccm. of 0.01 normal paranitrophenol solution and 9.5 ccm. of 0.01 normal KOH solution to 100 ccm. of water. *a.* Calculate the indicator-constant, neglecting the quantity of the acetic acid displaced from its salt by the small proportion of paranitrophenol present. *b.* Show what percentage error is made in (H^+), and therefore in K_I, by neglecting this displaced quantity.

Prob. 41. Determination of Small Hydrogen-Ion Concentrations by Means of Indicators.—When a small proportion of phenol phthalein $(K_I = 10^{-10})$ is added to a 0.1 formal solution of NaHCO$_3$ at 25° the indicator is found by color comparisons to be 6.0% transformed into its salt. Calculate the hydrogen-ion and hydroxide-ion concentration in the solution.

Titration of Acids and Bases.—

Prob. 42. 100 ccm. of a 0.2 normal solution of an acid whose ionization-constant is 10^{-5} are titrated at 25° (where the ionization-constant of water K_W is 10^{-14}) with 0.2 normal KOH solution. Calculate the hydrogen-ion concentration (H^+) in the mixture when 99.0, 99.5, 99.8, 100.0, 100.2, 100.5, and 101.0 ccm. of the KOH solution have been added.

Prob. 43. The values of (H^+) obtained in Prob. 42 and those calculated in the same way for acids whose ionization-constants (K_A) are 10^{-3}, 10^{-7}, and 10^{-9} for different ratios (B/A) of the quantity of 0.2 normal KOH to the quantity of 0.2 normal acid are at 25° as follows:

Ratio	Values of the hydrogen-ion concentration for			
B/A	$K_A = 10^{-3}$	$K_A = 10^{-5}$	$K_A = 10^{-7}$	$K_A = 10^{-9}$
0.980	2×10^{-5}	2×10^{-7}	2×10^{-9}	2.4×10^{-11}
0.990	1×10^{-5}	1×10^{-7}	1×10^{-9}	1.6×10^{-11}
0.995	5×10^{-6}	5×10^{-8}	5×10^{-10}	1.2×10^{-11}
0.998	2×10^{-6}	2×10^{-8}	2.4×10^{-10}	1.1×10^{-11}
1.000	1×10^{-6}	1×10^{-9}	1×10^{-10}	1.0×10^{-11}
1.002	5×10^{-11}	5×10^{-11}	4×10^{-11}	0.9×10^{-11}
1.005	2×10^{-11}	2×10^{-11}	2×10^{-11}	0.8×10^{-11}
1.010	1×10^{-11}	1×10^{-11}	1×10^{-11}	0.6×10^{-11}
1.020	5×10^{-12}	5×10^{-12}	5×10^{-12}	0.4×10^{-11}

These numbers are also the values of (OH^-) for the case that a 0.2 normal solution of a base having an ionization-constant equal to 10^{-3}, 10^{-5}, 10^{-7}, or 10^{-9} is titrated with a 0.2 normal solution of a strong acid (like HCl), provided the numbers in the first column denote the ratio (A/B) of the quantity of acid to the quantity of base. (Thus, when the ratio A/B is 0.98, the value of (OH^-) is 2×10^{-5} for a base for which $K_B = 10^{-3}$.)

a. Plot the common logarithms of these values of (H^+) as ordinates against the corresponding values of the ratio of base to acid as abscissas, for each of the four acids. *b.* On the right-hand side of the same diagram write in a scale of values of $\log_{10}(OH^-)$ corresponding to the values of $\log_{10}(H^+)$ on the left-hand side; and at the top of the diagram write in a scale of ratios of acid to base (A/B) corresponding to the scale of ratios of base to acid at the bottom (thus, B/A = 0.98 corresponds to A/B = 1.02). Now make plots on the same diagram showing how (H^+) or (OH^-) varies in titrating bases of ionization-constants 10^{-3}, 10^{-5}, 10^{-7}, and 10^{-9} with HCl at 25°, similar in all respects to the plots previously made for the four acids.

Prob. 44. *a.* From a study of the diagram of Prob. 43 tabulate the values between which the indicator-constant must lie in order that the titration of each of the four acids and four bases may be correct within 0.2%, assuming that the indicator is 9% transformed. *b.* Show from the plot what percentage error would be made in using phenol

phthalein ($K_I = 10^{-10}$) in titrating an acid for which $K_A = 10^{-5}$ when the fraction of the indicator transformed is 1%, 9%, and 50%; also in titrating an acid for which $K_A = 10^{-7}$ when the fraction of the indicator transformed is 9% and 50%. *c.* If the acid for which $K_A = 10^{-9}$ were titrated with the aid of an indicator for which $K_I = 0^{-12}$ (which is not far from the value for trinitrobenzene), what error would be made when the fraction of the indicator transformed is 5%, 9%, and 15% transformed? (Note that in a titration carried out in the usual way the fraction transformed is not determined more closely than this. Note also that an error in the assumed value of the indicator-constant would affect the results in the same way as a variation in the fraction transformed.)

Prob. 45. Calculate the value of (H^+) at the end-point in titrating with phenol phthalein ($K_I = 10^{-10}$) when the fraction of it transformed x is 5% and 20%; with rosolic acid ($K_I = 10^{-8}$) when $x = 5$% and 20%; with paranitrophenol ($K_I = 10^{-7}$) when $x = 1$% and 20%; and with methyl orange ($K_I = 5 \times 10^{-4}$) when $x = 80$% and 95% (these being about the limits practicable in a titration). Draw in on the diagram made in Prob. 43 horizontal lines representing these limiting values of (H^+) for the four indicators. Letter the curves and lines on the diagram so as to show what each represents.

Prob. 46. With the aid of the diagram show which of these indicators would give a result accurate within 0.2–0.3% in titrating *a,* NH_4OH with HCl; *b,* HNO_2 with KOH; *c,* aniline ($K_B = 4 \times 10^{-10}$) with HCl.

REACTIONS INVOLVING SOLID SUBSTANCES

90. Form of the Mass-Action Expression.—When a substance present as a solid phase is involved in a reaction with gaseous substances at small pressures, it has in the gaseous phase of all equilibrium mixtures at any definite temperature the same pressure, namely, one equal to the vapor-pressure of the solid substance. Similarly, when a substance present as a solid phase is involved in a reaction with dissolved substances at small concentrations, it has in the liquid phase of all equilibrium mixtures at any definite temperature, the same concentration, namely, one equal to its concentration in a solution saturated with the solid substance and containing no other solutes. Hence the pressure in the gaseous phase or the concentration in the liquid phase of any substances which are also present as solid phases may be left out in formulating the mass-

action expression; their constant pressures or concentrations being understood to be included in the equilibrium-constant. Thus, the mass-action expression for the reaction* $Fe + H_2O = FeO + H_2$ is simply $p_{H_2}/p_{H_2O} = K$.

91. Reactions involving Solid and Gaseous Substances.—The simplest type of the reactions involving solid and gaseous substances is that in which only one substance is present in appreciable quantity in the gaseous phase. Examples of this type are: $2Ag_2O = 4Ag + O_2$; $CaCO_3 = CaO + CO_2$; and $CaSO_4.2H_2O = CaSO_4 + 2H_2O$. The mass-action expression for this case is simply $p = K$, which signifies that at any definite temperature there is only one pressure of the gas at which there can be equilibrium. This pressure is called the *dissociation-pressure* of the substance undergoing decomposition (thus of the silver oxide, the calcium carbonate, or the gypsum). If the pressure of the gas is kept larger than this pressure, the reaction takes place completely in one direction, with the result that the gas is entirely absorbed; and if the pressure is kept smaller, the reaction takes place completely in the other direction, with the result that the dissociating substance completely decomposes. This important characteristic of reactions of this type will be fully considered in the next chapter.

Other types of reactions involving solid and gaseous substances are illustrated by Probs. 47–51.

Prob. 47. When solid NH_4SH is placed in a vacuous space at 25° a pressure of 500 mm. is developed, owing to the dissociation of the salt, which is itself not appreciably volatile, into NH_3 and H_2S. What increase of pressure would take place if solid NH_4SH were introduced into a space which already contained hydrogen sulphide at a pressure of 300 mm.?

Prob. 48. The equilibrium-constant (expressed in atmospheres) of the reaction $2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O$ at 100° is 0.23. A current of moist carbon dioxide is passed at 1 atm. over solid sodium hydrogen carbonate (in order to free it from adhering water). How great must the mol-fraction of the water in the gas be to prevent decomposition of the salt?

Prob. 49. A current of air at 1 atm. is passed over carbon at 1000°. What will be the molal ratio of CO_2 to CO in the issuing gas,

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*Solid substances occurring in chemical equations are represented by black letters and gaseous substances by italics, whenever it is important to indicate the state of aggregation.

assuming equilibrium to be reached? The equilibrium-constant for the reaction $C + CO_2 = 2CO$ at 1000° is 140.

Prob. 50. At 1120° the gaseous mixture in equilibrium with iron and ferrous oxide consists of 54 mol-percent H_2 and 46 mol-percent H_2O. Calculate the dissociation-pressure of ferrous oxide. (Refer to Probs. 8 and 9.)

Prob. 51. In the blast-furnace process iron is reduced by the reaction $FeO + CO = Fe + CO_2$. Calculate the least quantity of carbon monoxide that could reduce one formula weight of FeO at 1120°, using the dissociation-pressure of ferrous oxide found in Prob. 50.

92. Reactions involving Solid and Dissolved Substances.

Prob. 52. At 25° the solubility of iodine in water is 0.0013 molal; and its solubility in 0.1 normal KI solution is 0.0517 molal, the increase being due to the reaction $K^+I^- + I_2 = K^+I_3^-$. Calculate its solubility in 0.01 normal KI solution at 25°.

Prob. 53. Hypochlorous acid is prepared by the action of chlorine solution on solid mercuric oxide. What is the expression for the equilibrium of the reaction?

93. Solubility Effects in the Case of Largely Ionized Substances.

—The mass-action law evidently requires, in all dilute solutions saturated with the same solid substance, that the concentration of the unionized substance have the same value, and also that the product of the concentrations of its ions have the same value, whatever other substances may be present (at small concentrations) in the solution. Owing, however, to the considerable deviations from the mass-action law (referred to in Art. 86) which largely ionized substances exhibit even at moderately small concentrations, it is clear that one or both of these principles must be inexact when applied to such substances. Experiment has shown that, in this case as in others, a fairly good agreement with the facts is secured (up to about 0.2 normal) by employing the principle involving the ions— that expressing the constancy of the ion-concentration product.

In solutions saturated with tri-ionic substances, such as silver sulphate or calcium hydroxide, the relations are further complicated, except in very dilute solutions, by the probable presence in considerable proportion of intermediate ions, such as $AgSO_4^-$ or $CaOH^+$. Owing to lack of knowledge of the proportion in which such ions are present, the principle of the constancy of the ion-concentration product (for example, of the products $(Ag^+)^2 \times (SO_4^=)$ and $(Ca^{++}) \times (OH^-)^2$), combined with the assumption that the conductance-ratio

gives the ionization of the salt into the simple ions, can be used with fairly satisfactory results only when the solubility of the solid substance and the concentration of any other substance present are both very small.*

Solubility-Decrease by Substances with a Common-Ion.—

Prob. 54.　a. Derive an expression for the solubility s of silver chloride in a dilute sodium chloride solution of concentration c in terms of its solubility s_0 in water, assuming the salts to be completely ionized.　*b.* Calculate the ratio s/s_0 for $c = s_0$, for $c = 2s_0$, and for $c = 10s_0$.

Prob. 55. The solubility at 25° of thallous chloride (TlCl) is 0.0161 normal.　Calculate its solubility in a 0.05 normal solution of potassium chloride.　Estimate the ionization-values involved with the aid of the average values for uniunivalent salts given in Art. 86. Compare the calculated solubility with the value (0.00592 normal) found by experiment.

Prob. 56. The solubility of magnesium hydroxide in water at 18° is 1.4×10^{-4} formal.　*a.* Calculate its solubility in 0.002 formal NaOH solution.　*b.* Calculate its solubility in 0.001 formal $MgCl_2$ solution. (Assume that the substances are completely ionized.)

*Prob. 57.—Solubility-Increase through Complex-Formation.—*The solubility of silver chloride in water at 25° is 1.1×10^{-5} formal.　Calculate its solubility in 0.1 formal NH_3 solution.　There is formed a complex ion by the reaction $Ag^+ + 2NH_3 = Ag(NH_3)_2{}^+$, its equilibrium-constant (commonly called the complex-constant) having the value 1.4×10^7.　Assume the ionization of the salts to be complete, and make any other justifiable simplification.

*Prob. 58.—Solubility-Increase through Metathesis.—*The solubility of magnesium hydroxide in water at 18° is 1.4×10^{-4} formal.　Calculate its solubility in 0.002 formal NH_4Cl solution.　Assume that the salts and the magnesium hydroxide are completely ionized.　Neglect the concentration of OH^- in comparison with that of NH_4OH.

Conversion of One Solid Substance into Another.—

Prob. 59. The solubility of silver thiocyanate is 1.2×10^{-6} formal and that of silver bromide is 0.6×10^{-6} formal at 25°.　*a.* Calculate the equilibrium-constant of the reaction $AgSCN + K^+Br^- = AgBr + K^+SCN^-$

How small these concentrations must be in order that the solubility in the presence of an added salt may be calculated from that in water with an accuracy of a few percent depends on the valence type of the added substance. When this substance has the same univalent ion as the substance saturating the solution (e. g., when $Ag^+NO_3^-$ is added to $Ag^+_2SO_4^=$, or Na^+OH^- to $Ca^{++}(OH^-)_2$), the total concentration may be as high as 0.05 normal; but when the added substance has the same bivalent ion (e. g., when $K_2^+SO_4^=$ is added to $Ag^+_2SO_4^=$ or $Ca^{++}(NO_3^-)_2$ to $Ca^{++}(OH^-)_2$) the total concentration must not be greater than 0.002 normal.

in dilute solution. *b.* If 8.3 g. of solid silver thiocyanate are treated with 200 cc. 0.1 formal KBr solution, what proportion of the silver salt is converted into bromide? *c.* What volume of the 0.1 formal KBr solution would convert the silver thiocyanate completely into bromide? *d.* With what solutions of potassium thiocyanate and potassium bromide could the silver thiocyanate be treated without any change taking place?

Prob. 60. Determine the ratio of carbonate to hydroxide in the solution obtained by digesting at 25° a 0.1 formal Na_2CO_3 solution with excess of solid $Ca(OH)_2$ (as in the technical process of causticizing soda). The solubility of calcium hydroxide is 0.020 formal, and the product $(Ca^{++}) \times (CO_3^=)$ has the value 3×10^{-9} in water saturated with calcium carbonate. Assume that the substances are completely ionized.

EQUILIBRIUM OF CHEMICAL SYSTEMS IN RELATION TO THE CHARACTER OF THE PHASES PRESENT

94. Fundamental Conceptions.—In this chapter are considered the principles relating to the number, state of aggregation, and composition of the phases (defined as in Art. 23) which coexist in equilibrium with one another when a given substance is subjected, or when mixtures in various proportions of two or more given substances are subjected, to different temperatures and pressures.

The kinds of phenomena to be considered are illustrated by the following examples. The state in which the substance water exists is determined by the temperature and pressure—thus, whether it exists in the form of a single phase as ice, as liquid water, or as vapor; in the form of two phases as ice and liquid water, as ice and vapor, or as liquid water and vapor; or in the form of the three phases, ice, liquid water, and vapor. So also in the case of two substances, such as carbon bisulphide and acetone, there are, as shown by the vapor-pressure–composition and boiling-point–composition diagrams of Arts. 32 and 33, definite conditions of pressure and temperature at which any definite mixture of the two substances forms two phases— a liquid phase and a vapor phase; and under these conditions the composition of each phase is also definite.

Certain fundamental conceptions may first be presented.

The combination of matter under consideration is called the *system.* A system is therefore defined when the nature and quantity of the substances of which it is composed are specified. Throughout this chapter are to be considered the conditions which determine the state of systems in equilibrium composed of the same kinds of substances in various proportions; that is, of a series of systems having the same qualitative, but varying quantitative composition.

Any pure substances (Art. 2) which, put together in suitable proportions, will produce each and every phase with such varying composition as it may have in the systems under consideration are called the *components,* the pure substances being so chosen that the systems can be produced out of the *smallest* number of them.

Any phase may be produced out of the components either directly or as a result of equilibria established between them. For example, a gaseous phase containing hydrogen, oxygen, and water-vapor at high temperatures where chemical equilibrium is established between these substances can be produced by putting together only hydrogen and oxygen; and the phase is therefore said to consist of these two components. Such a gaseous phase at low temperatures, where no chemical reaction takes place between the hydrogen and oxygen, can be produced only by putting together with these two substances also water; so that in this case the phase is said to consist of these three components. It will be clear from this example that the number of components is determined not only by the substances present, but also by the equilibria which are established between them.

Another aspect of the matter may be considered. In a gaseous phase where hydrogen, oxygen, and water are in chemical equilibrium, one particular system could be produced by taking only the one substance water; but the phase considerations of this chapter have reference always to a series of systems of the same qualitative, but varying quantitative composition; and such a series containing hydrogen, oxygen, and water-vapor in every possible proportion cannot be produced out of water alone, but can be produced out of hydrogen and oxygen. As another example consider a gaseous phase containing HCl, O_2, Cl_2, and H_2O. By taking HCl and O_2 as two components, the other two substances can be produced out of them by the reaction $O_2 + 4HCl = 2Cl_2 + 2H_2O$, but only in equivalent proportions. To produce a system containing the four substances in any proportion whatsoever, it is necessary to make use of a third component, either Cl_2 or H_2O. Thus, either by adding Cl_2 to a mixture containing O_2 and HCl in any proportions and Cl_2 and H_2O in equivalent proportions, or by removing Cl_2 from such a mixture, any composition whatever can evidently be secured. The systems are therefore said to consist of three components. In the above description O_2, HCl, and Cl_2 have been used as the components; but evidently any other three of the four substances might be equally well employed. It is, however, preferable to select as components substances of as simple a composition as possible; thus in this case, O_2, HCl, and Cl_2 rather than O_2, HCl, and H_2O.

Prob. 1. With the aid of the preceding considerations, specify the components which will produce phases containing the following chemical substances, assuming chemical equilibrium to be established between them. In answering this question, write chemical equations showing how all the chemical substances can be produced from the pure substances used as components. *a.* Gaseous H_2, O_2, CO, CO_2, H_2O. *b.* Solution containing H_2O, $(H_2O)_2$, $NaCl \cdot 2H_2O$, $NaCl$, Na^+, Cl^-. *c.* Solution containing H_2O, NH_4CN, NH_4^+, CN^-, NH_3, NH_4OH, HCN.

Prob. 2. Specify the components of the systems that exist in the following groups of phases, assuming chemical equilibrium to be established between the substances named: *a.* Solid NH_4Cl, gaseous NH_3 and HCl. *b.* Solid $CaCO_3$, solid CaO, gaseous CO_2. *c.* Solid $MgSO_4 \cdot 7H_2O$, solid $MgSO_4 \cdot 6H_2O$, solution of $Mg^{++}SO_4^=$ in water, water-vapor. *d.* Solid carbon; gaseous H_2O, H_2, CO, and CO_2. *e.* Solid iron, solid FeO, gaseous CO and CO_2. *f.* Solid iron, solid FeO, solid carbon, gaseous CO and CO_2.

It is a fundamental law of the equilibrium between phases that the absolute quantity of the different phases does not influence their composition. Thus the composition of a solution in equilibrium with a solid salt is not dependent on the quantity of the solid in contact with the solution. The composition of the vapor in equilibrium with a definite liquid solution is not dependent on the quantities of liquid and vapor in contact with one another. The proportion of hydrogen and water-vapor in equilibrium with solid iron and solid ferrous oxide is not dependent on the quantities of these solid phases in contact with the gaseous phase. The *rate* at which equilibrium is established between phases is, however, greatly increased by increasing the extent of the surfaces between them.

A system is determined by its composition, that is, by the quantities of its components, as described in the preceding paragraphs. The *state* of a system is determined when the nature and quantity of each of its different phases are specified and when the specific properties of each phase, such as its density, specific conductance, index of refraction, etc., have definite values. In order to determine fully the specific properties of any one phase of a system, it is necessary to specify, in addition to the proportions of its components, any external factors which affect these properties. The only external factors which commonly have an appreciable influence are the pressure and temperature; and, in the following considerations relating to the equilibrium of phases, these factors alone are taken into account, and their values are assumed to be uniform throughout all the phases of a system.

Briefly stated, the purpose of this chapter is to show how the nature, the quantity, and the composition of the phases of a system may be represented when the composition of the system as a whole and the pressure and temperature are given.

Systems are classified according to the number of their components. In this chapter one-component systems are first considered; then a general principle, known as the phase rule, applicable to systems with any number of components, is presented; and finally two-component and three-component systems are discussed.

ONE–COMPONENT SYSTEMS

95. Representation of the Equilibrium-Conditions by Diagrams.— In the case of one-component systems the conditions under which the different phases exist in equilibrium with each other are conveniently represented by pressure-temperature diagrams; for the state of any phase of such a system is evidently determined when the pressure and temperature are specified.
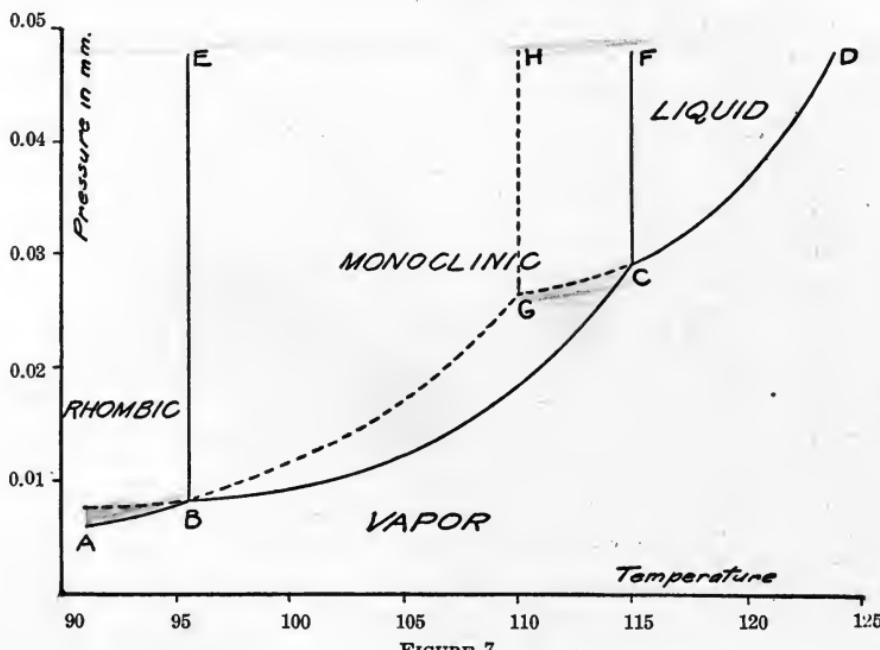
FIGURE 7

Figure 7 shows a part of the temperature-pressure diagram for the component sulphur, which forms not only liquid and gaseous phases, but also two solid phases, known from their crystalline forms

as rhombic and monoclinic sulphur. In the diagram the (vapor-pressure) curve AB represents the pressures at which rhombic sulphur and sulphur-vapor are in equilibrium at various temperatures; the (vapor-pressure) curve BC represents the pressures at which monoclinic sulphur and sulphur-vapor are in equilibrium at various temperatures; and the (transition-temperature) curve BE represents the temperatures at which monoclinic and rhombic sulphur are in equilibrium at various pressures. Temperatures, like these, at which two solid phases are in equilibrium with each other are called *transition-temperatures*.

The point of intersection B of these three curves shows the only temperature and pressure at which rhombic sulphur, monoclinic sulphur, and sulphur-vapor are in equilibrium with one another. A point, like this, at which three phases coexist is called a *triple point*.

The (vapor-pressure) curve CD represents the pressures at which liquid sulphur and sulphur-vapor are in equilibrium with each other at various temperatures; and the (melting-point) curve CF represents the temperatures at which monoclinic sulphur and liquid sulphur are in equilibrium at various pressures. The point C is evidently a second triple point at which monoclinic sulphur, liquid sulphur, and sulphur-vapor co-exist. As indicated on the diagram, the fields between the different lines show the conditions under which the sulphur exists as a single phase.

Prob. 3. Describe with the aid of the diagram the changes that take place, *a*, when sulphur is heated in an evacuated tube in contact with its vapor from 90° to 125°; *b*, when sulphur is allowed to cool from 125° to 90°, the pressure being kept constant at 0.04 mm.

The curves BE and CF in Figure 7 are very nearly vertical lines; for increase of pressure always produces a relatively small change in the transition or melting temperature. Thus the transition-temperature of the two solid forms of sulphur increases about 0.04°, and the melting-point of monoclinic sulphur increases about 0.03°, per atmosphere of pressure. With certain substances the effect of pressure is to decrease the transition or melting temperature; thus the melting-point of ice is lowered by 0.0076° by an increase of pressure of one atmosphere.

Prob. 4. At what temperature and pressure is there a triple point in the system composed of water? The freezing-point at 1 atm. is 0°. For the other data needed refer to Art. 34 and the preceding text.

96. Unstable Forms.

Prob. 5. *a.* To what equilibria do the curves BG, GC, and GH and the point G in Figure 7 correspond? *b.* Considered with reference to these equilibria, to what form of sulphur do the fields EBGH, HGCF, and GBC correspond? *c.* In what sense are these equilibria unstable?

Prob. 6. Draw a sulphur diagram extending to pressures above the triple-point between rhombic, monoclinic, and liquid sulphur, which lies at 151° and 1280 atm.

Prob. 7. It will be noted that the unstable form at any temperature has the greater vapor-pressure. Prove that this must be so by showing what would happen if the two forms were placed beside each other in an evacuated apparatus.

Prob. 8. Prove by a similar consideration that the unstable form must also have the greater solubility in any solvent, such as carbon bisulphide. (Note that a substance is commonly present in the same molecular form in the solutions produced by dissolving its different solid forms.)

How great the tendency is for a substance to remain in the same form after passing through a melting-temperature or transition-temperature and thus to exist in an unstable form depends in large measure on the nature of the substance. The following general statements in regard to it can, however, be made. A crystalline solid cannot as a rule be heated appreciably above its melting-point; thus, ice always melts sharply at 0° (under a pressure of 1 atm.). On the other hand, a liquid (like water) can ordinarily be cooled to a temperature considerably below the freezing-point if agitation and intimate contact with solid particles, especially with the stable solid phase, is avoided. Still more pronounced is the tendency of solid substances to remain in the same form upon being heated or cooled through a transition-temperature; thus rhombic sulphur can be heated to its melting-point (110°), although this is about 15° higher than the transition-temperature (95.5°) at which it should go over into monoclinic sulphur; and monoclinic sulphur can be cooled to room temperature without going over into the rhombic form, provided this be done quickly and without agitation. The rate at which an unstable phase goes over into the stable

one tends to increase with the distance from the transition-temperatures; but when the substance is below its transition-temperature this tendency may be more than compensated by the greatly reduced rate of reaction which a considerable lowering of temperature always produces; thus white phosphorus is an unstable form, but the rate at which it goes over into the stable red form at room temperature is so small that it may be preserved unchanged for years; similarly, diamond is an unstable form of carbon at room temperature, but it does not go over into graphite or amorphous carbon.

An effective means of causing an unstable form to go over into a stable one is to mix it intimately with the stable form. The transition may be further accelerated by moistening the mixture of the two forms with a solvent in which they are somewhat soluble. These facts are made use of in the determination of transition-temperatures. Thus the transition-temperature of sulphur has been determined by charging a bulb with a mixture of rhombic and monoclinic sulphur, filling it with carbon bisulphide and oil of turpentine, keeping it for an hour first at 95° and then at 96°, and noting whether the liquid rose or fell in the capillary stem attached to the bulb. The volume was found to decrease steadily at 95° (owing to the transition of the monoclinic into the rhombic form), and to increase steadily at 96° (owing to the reverse transition), showing that the transition-temperature lies between 95 and 96°.

Prob. 9. Suggest an explanation of the catalytic action of the solvent in accelerating the transition of the sulphur.

Prob. 10. Outline a method by which the transition-temperature of sulphur could be determined by quantitative solubility measurements.

THE PHASE RULE

97. Concept of Variance.

Prob. 11. If sulphur is kept at a specified pressure of 0.04 mm., at what temperatures is it stable, *a*, in a single phase as rhombic sulphur, as monoclinic sulphur, and as liquid sulphur? *b*, in two phases, as rhombic and monoclinic sulphur, and as monoclinic and liquid sulphur? *c*, in the three phases, rhombic sulphur, monoclinic sulphur, and sulphur-vapor?

It will be noted that, in order to determine the position on the diagram and therefore the state of the system, the values of two

determining factors, namely, the values of both the pressure and the temperature, must be specified when there is only one phase; that the value of only one of these factors, either the temperature or pressure, need be specified when any two phases coexist; and that no condition can be arbitrarily specified when any three phases coexist.

The number of determining factors whose values can and must be specified in order to determine the state of a system consisting of definite phases and components is called its *variance**; and, corresponding to the number of such factors, systems are said to be *nonvariant, univariant, bivariant,* etc.

It is evident from the preceding statements that when a one-component system consists of only one phase the system is bivariant, when it consists of two phases it is univariant, and when it consists of three phases it is nonvariant. In other words, the sum of the variance and number of phases is always three for a one-component system.

Prob. 12. Discuss with reference to the principle just stated and to the sulphur diagram the possibility of the coexistence, *a,* of the three phases, rhombic, monoclinic, and liquid sulphur; *b,* of the four phases, rhombic, monoclinic, liquid, and gaseous sulphur.

98. Inductive Derivation of the Phase Rule.

Prob. 13. In order that the specific properties of a liquid mixture of ethyl alcohol and water, such as its density, specific heat-capacity, or refractive index, may have definite values, we must evidently state not only that it is at some definite temperature and pressure (say 20° and 1 atm.), but also that it contains some definite proportion of alcohol or water (say 30% of alcohol). What is the variance of a system consisting of such a mixture? What are the number of phases and the number of components?

Prob. 14. In the case of each of the following systems, state of what factors the values might be specified in order that all its specific properties may be fully determined; and state the number of components, the number of phases, and the variance of the system: *a.* Two solutions produced by shaking together water and bromine. *b.* The two solutions of water and bromine and their vapors. *c.* The two solutions of water and bromine, their vapors, and ice. *d.* A solution of water,

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*Some authors use the expression *degrees of freedom,* instead of the term *variance.*

ethyl alcohol, and acetic acid. *e.* A solution of water, ethyl alcohol, and acetic acid and their vapors.

Prob. 15. *a.* Make a table showing the number of components, the number of phases, and the variance of each of the systems named in Probs. 11, 13, and 14. *b.* State the effect of increasing the number of phases in a system consisting of a definite number of components. *c.* State the effect of increasing the number of components in a system with a definite number of phases. *d.* Add to the table a column showing the sum of the number of phases and of the variance for each of the systems.

These problems show that in every case the sum of the number of phases (**P**) and of the variance (**V**) is greater by two than the number of the components (**C**); that is, **P + V = C + 2.** This principle, which is called the *phase rule,* is a general one, applicable to systems consisting of any number of components and of any number of phases.

The phase rule furnishes a basis for the classification of different types of equilibrium. It also enables the number of phases that can exist under specified conditions to be predicted. The usefulness of the phase rule itself is, however, often exaggerated. Of primary importance in the treatment of the equilibrium conditions of systems in relation to the phases present are the methods of representing those conditions by diagrams, as described in later articles of this chapter.

Prob. 16. Sodium carbonate and water form solid hydrates of the composition $Na_2CO_3.H_2O$, $Na_2CO_3.7H_2O$, and $Na_2CO_3.10H_2O$. *a.* How many of these hydrates could exist in equilibrium with the solution and ice under a pressure of 1 atm.? *b.* How many of these hydrates could exist in equilibrium with water-vapor at 30°?

99. Derivation of the Phase Rule from the Perpetual-Motion Principle.*—In order to determine fully the state of one-phase systems consisting of any number **C** of components (as defined in Art. 94), evidently the composition of the phase and in addition any external factors that determine its properties must be specified. The composition of the phase is fully determined by specifying the mol-fractions of all but one of the components, that is, by specifying **C — 1** quantities. The only external factors which commonly affect the properties of a phase of specified composition are temperature and pressure; but in special cases certain other factors, some of which are mentioned below, have an appreciable influence. Representing the number of

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* This Article may be omitted in briefer courses.

such external determining factors by n, the variance or total number of quantities (independent variables) that must be specified is $\mathbf{C} - 1 + n$. In this case, therefore, where the number of phases $\mathbf{P}$ is one, the sum of the number of phases and the variance $\mathbf{V}$ is equal to $\mathbf{C} + n$; that is, $\mathbf{P} + \mathbf{V} = \mathbf{C} + n$; or, for the common case where pressure and temperature are the only external determining factors, $\mathbf{P} + \mathbf{V} = \mathbf{C} + 2$. For example, the state of one-phase systems consisting of three components (1, 2, 3) is fully determined by specifying four quantities, namely, the mol-fractions (x_1 and x_2) of any two of the components and the pressure (p) and temperature (T); hence any specific property whatever of the system, such as its density d, can be expressed as some function of these four variables, such as $d = f(x_1, x_2, p, T)$. In the general case, where the number of components is $\mathbf{C}$ and the number of external factors is n, the function becomes

$$d = f(x_1, x_2, \ldots x_{c-1}, p, T, \ldots).$$

The derivation of the phase-rule now consists in showing that the equation $\mathbf{P} + \mathbf{V} = \mathbf{C} + n$, which for one-phase systems is a result of the definitions of components and of external factors, still holds true whatever be the number of phases. In order that this may be so, it is evidently necessary only that each new phase introduced into the system shall diminish the variance by one; for then $\mathbf{P} + \mathbf{V}$ will still have its former value $\mathbf{C} + n$. That this is the case can be shown as follows.

Consider that a system of $\mathbf{C}$ components (1, 2, 3, .. $\mathbf{C}$) exists as a gaseous phase, and that a new, liquid or solid, phase is developed in it (for example, by varying the pressure or temperature). Now the partial pressures ($p_1, p_2, \ldots p_c$) of the separate components in the gaseous phase are, like any other property of the phase, functions only of the mol-fractions ($x_1, x_2, \ldots x_{c-1}$) and of the external factors ($p, T, \ldots$). This conclusion may be expressed mathematically as follows:[*]

$$p_1 = f_1(x_1, x_2, \ldots x_{c-1}, \boldsymbol{p}, \boldsymbol{T}, \ldots).$$
$$p_2 = f_2(x_1, x_2, \ldots x_{c-1}, p, T, \ldots).$$
$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$
$$p_c = f_c(x_1, x_2, \ldots x_{c-1}, p, T, \ldots).$$

[*] In the case of perfect gases, functions of the simpler form $p_1 = x_1 p$ hold true; but the other variables $x_2, \ldots T, \ldots$ affect p_1 when the gases do not conform to the perfect-gas law.

When the new, liquid or solid, phase is present in equilibrium with the gaseous phase, the partial pressure of each component in the gaseous phase is determined by the mol-fractions $(x_1', x_2', \ldots x'_{c-1})$ of the liquid or solid phase, by the temperature, and by any other external determining factor which has an appreciable influence; for, if a liquid or solid phase of such composition as to be in equilibrium with the gaseous phase could also be in equilibrium at the same temperature with some other gaseous phase with different partial pressures, perpetual motion of the kind described in Art. 28 could be realized. This conclusion from the perpetual-motion principle that the partial pressures must be fully determined by the mol-fractions in the liquid phase and by the external factors may be expressed mathematically as follows:

$$p_1 = f_1'(x_1', x_2', \ldots x'_{c-1}, p, T, \ldots).$$
$$p_2 = f_2'(x_1', x_2', \ldots x'_{c-1}, p, T, \ldots).$$
$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$
$$p_c = f_c'(x_1', x_2', \ldots x'_{c-1}, p, T, \ldots).$$

By equating these two sets of expressions for $p_1, p_2, \ldots p_c$, the following functional relations between the mol-fractions in the gaseous phase and those in the liquid phase are obtained:

$$f_1(x_1, x_2, \ldots x_{c-1}, p, T, \ldots) = f_1'(x_1', x_2', \ldots x'_{c-1}, p, T, \ldots).$$
$$f_2(x_1, x_2, \ldots x_{c-1}, p, T, \ldots) = f_2'(x_1', x_2', \ldots x'_{c-1}, p, T, \ldots).$$
$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$
$$f_c(x_1, x_2, \ldots x_{c-1}, p, T, \ldots) = f_c'(x_1', x_2', \ldots x'_{c-1}, p, T, \ldots).$$

That is, the new phase gives us **C** new functional equations in which only **C**—1 new variables (namely, $x_1', x_2', \ldots x'_{c-1}$) are introduced. By combining these new equations with each other the new variables may evidently be eliminated, yielding a functional relation of the form:

$$f'(x_1, x_2, \ldots x_{c-1}, p, T, \ldots) = 0.$$

This is obviously a relation between the **C** $- 1 + n$ variables which determine any property of the gaseous phase, in the way described in the first paragraph of this Article. Hence the number of these variables whose values can and must be specified to determine the properties of the gaseous phase is one less than it was when that phase was alone present. And in a similar way this can be shown to be true also of the properties of the liquid or solid phase. In other words, the new phase diminishes the variance of the system by one, and the sum

$P + V$ retains the value $C + n$ which it had when the system consisted of a single phase. And evidently, since each additional phase formed within the system will similarly decrease the variance by one, the sum $P + V$ will always have the same value $C + n$.

In the above derivation it was assumed that a gaseous phase was present in the system. It will be noted, however, that the partial pressures in the gaseous phase were employed only as a means of deriving functional relations between the mol-fractions of the components in two different phases, and that the partial pressures disappeared in these relations. This indicates, and it can be rigorously shown, that functional relations between the mol-fractions of the same form as those given above hold true for any pair of phases; for example, for two liquid phases. It follows therefore that the phase rule is applicable to any kind of system whatever, in the form $P + V = C + n$.

As has been stated, the value of n in the above derived expression of the phase rule is commonly 2; for the only external factors that ordinarily influence appreciably the state of the system are temperature and pressure. In some cases, however, other factors come into play. For example, this is sometimes true of intensity of illumination or of electric or magnetic field. Thus illumination of silver chloride increases its dissociation-pressure; and an electric discharge through an equilibrium mixture of nitric oxide, nitrogen, and oxygen increases the proportion of nitric oxide in the mixture. Another factor which makes the value of n greater than 2 is introduced when different pressures are applied by means of semipermeable walls to different phases of the system. Thus the pressure of the vapor in equilibrium with a liquid is progressively increased when the liquid is subjected to an increasing pressure by means of a piston permeable for the vapor only. A common case of this kind is that where the atmosphere acts as such a piston, exerting a pressure on the liquid and solid phases of the system, but not on the components in the vapor phase.

TWO–COMPONENT SYSTEMS

100. Systems with Solid and Gaseous Phases.—The equilibrium of systems of this type at constant temperature has already been considered from the mass-action standpoint in Art. 91. Their equilibrium in relation to temperature and pressure is considered from the phase-rule standpoint in the following problems.

Prob. 17. Silver oxide dissociates fairly readily into silver and oxygen. *a.* Show from the phase rule that silver oxide can be heated in oxygen gas at a given pressure through a certain range of temperature without any decomposition taking place. *b.* Show also that there is one temperature, and only one, at which a mixture of silver oxide and silver can be kept under oxygen at the given pressure without any change taking place.

Prob. 18. The dissociation pressure of silver oxide is *0.1* atm. at 116°, *0.2* atm. at 132°, *1.0* atm. at 175°, and *2.0* atm. at 197°. *a.* If finely divided silver be heated in the air, what proportion of it will be finally converted into oxide when the temperature is 130°? when it is 140°? *b.* How could silver oxide be heated to 170° without any decomposition taking place?

Prob. 19. Describe a method by which pure oxygen can be prepared from the air with the aid of the reaction $2BaO_2 = 2BaO + O_2$.

Prob. 20. When a precipitate of hydrated manganese dioxide is ignited in the air it comes to a constant weight corresponding to the composition MnO_2 when the temperature is 450°, and to another constant weight corresponding to the composition Mn_2O_3 when the temperature is 500°; but when ignited in oxygen it changes to MnO_2 even at 500°. What do these facts show as to the dissociation-pressures?

Prob. 21. The dissociation-pressure of solid calcium carbonate

is	10	180	320	580	760	1000	mm.
at	600°	800°	840°	880°	896°	910°	

a. At what temperature will it begin to dissociate when it is heated in air free from carbon dioxide? *b.* At what temperature would it dissociate completely when heated in a covered crucible (so that there is equalization of the pressure, but no circulation of air into the crucible)? *c.* In lime-burning what temperature would have to be maintained in the kiln if there were no circulation of gases through it? What temperature would have to be maintained if the coal used as fuel were burned to carbon dioxide with the minimum quantity of air and the combustion-products were passed up through the kiln?

Prob. 22. A method has been suggested for the standardization of sulphuric acid solutions which consists in adding an excess of ammonia solution, evaporating, drying the residue at 100°, and weighing. In drying the salt some decomposition according to the reaction $(NH_4)_2SO_4 = NH_4HSO_4 + NH_3$ is likely to take place. How might the process be modified so as to hasten the drying and yet entirely prevent the decomposition?

101. Systems with Solid, Liquid, and Gaseous Phases. Pressure-Temperature Diagrams.—When a two-component system consists of three phases, the phase rule evidently shows that the specification of one of the determining factors (for example, the temperature) fixes the state of the system and therefore the values of the other factors (for example, of the pressure and of the composition of the liquid or the gaseous phase). The pressures at which the different groups of three phases exist in equilibrium at various temperatures can therefore be represented by lines on a diagram in which the pressure and temperature are taken as the coördinates.

Figure 8 shows a portion of the pressure-temperature diagram for a system consisting of the two components disodium hydrogen phosphate (Na_2HPO_4) and water (H_2O), for the case that the vapor-phase (V), which consists only of water-vapor, is always present. These two components are known to form the following solid phases: ice (I), anhydrous salt (A), dihydrate $Na_2HPO_4.2H_2O$ (AW_2), heptahydrate $Na_2HPO_4.7H_2O$ (AW_7), and dodecahydrate $Na_2HPO_4.12H_2O$ (AW_{12}); also a solution-phase (S) of variable composition, approaching pure water as one limit.

Prob. 23. Show from the phase rule how many phases, in addition to the vapor-phase, must be present in a two-component system in order that the pressure of the vapor may have a definite value at any given temperature.

Prob. 24. At 30° one formula-weight of Na_2HPO_4 is placed in contact with a large volume of water-vapor at 1 mm., and the volume of the vapor is steadily diminished (so slowly that equilibrium is established) until finally there remains in contact with the vapor only the saturated solution (which contains the components in the proportion $1Na_2HPO_4$: $33.2 H_2O$). State, with the aid of Figure 8, the changes that take place in the pressure of the vapor and the accompanying changes that take place in the character of the other phases in contact with it, throughout the whole process.

Prob. 25. Plot the pressure of the vapor (as ordinates) against the number of formula-weights of water absorbed by the salt as abscissas for the process described in Prob. 24 (up to the point where 15 formula-weights have been absorbed). Mark the lines on the plot so as to show what phases are present during each stage of the process.

Prob. 26. Make a plot like that of Prob. 25 for the case that the process described in Prob. 24 takes place at 38° (instead of at 30°).

Prob. 27. Describe a method of determining what hydrates of copper sulphate exist at 25°.

Prob. 28. Describe with the aid of Figure 8 what changes take place when a mixture of heptahydrate and dodecahydrate is heated from 30° to 38° in a sealed tube previously evacuated.

*Prob. 29.—Conditions under which Salts are Efflorescent or Hygroscopic.—*At 30° moist air is in contact with solid $Na_2HPO_4.7H_2O$. Under what conditions of humidity, *a*, would the salt remain unchanged? *b*, would it lose water? *c*, would it absorb water? (By the *humidity* of a gas is meant the ratio of the pressure of the water-vapor in the gas to the vapor-pressure of water at the same temperature.)
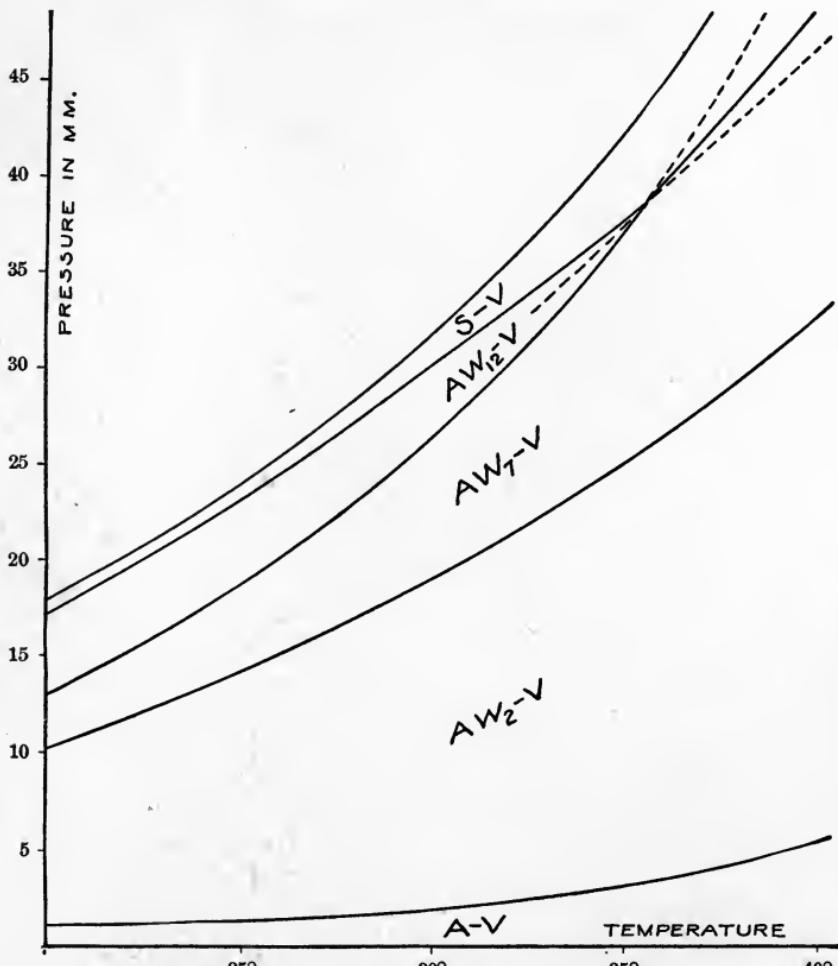
FIGURE 8

Prob. 30.—Preparation of Pure Hydrates.—a. State the conditions under which moist crystals of $Na_2HPO_4.12H_2O$ could be completely dried at 30° without any danger of decomposition. *b.* Describe a method by which these conditions could be practically realized.

Separation of Hydrates from Solutions.—

Prob. 31. State what solid phase separates on evaporating a dilute solution of Na_2HPO_4, *a*, at 30°, *b*, at 38°.

Prob. 32. The equilibrium-pressures (p) for the reaction $CaSO_4.2H_2O$ (gypsum) $=$ $CaSO_4$ (anhydrite) $+ 2H_2O$ and the vapor-pressures (p_0) of pure water at various temperatures (t) are as follows:

t	50°	55°	60°	65°
p	80	109	149	204 mm.
p_0	92	118	149	188 mm.

The solubility of calcium sulphate is so small that the vapor-pressure of its saturated solution may be considered to be identical with that of water. *a.* State what happens on heating gypsum from 50° to 65° in a sealed tube previously evacuated. *b.* State what solid phase separates when a solution of calcium sulphate is evaporated at 55°, and at 65°. *c.* State what solid phase would separate upon evaporating the solution at 55° if, when it became saturated, enough calcium chloride were added to reduce its vapor-pressure by 10%. Give the reasons in each case.

102. Systems with Solid and Liquid Phases. Temperature-Composition Diagrams.—The conditions under which three phases of a two-component system coexist may be also represented by a diagram in which the coördinates are the temperature and the composition of any phase in which both components are present in measurable quantities. Such diagrams are often employed when one of the phases is liquid.

From the phase-rule standpoint it is evident that the equilibrium conditions of a two-component system can still be represented by a temperature-composition diagram when the specification that the vapor-phase is present is replaced by the specification that the pressure has some definite value (greater than that at which the vapor can exist). Moreover, since pressure has, as illustrated in Art. 95, only a small effect on equilibria in which solid and liquid phases are alone involved, the lines on the temperature-composition diagram have substantially the same position when the system is under a pressure of one atmosphere as they do when it is under the pressure of the vapor. And in practice composition-temperature diagrams are ordinarily constructed from data determined under the atmospheric pressure.

The form of the temperature-composition diagram varies greatly with the character of the solid phases which the components are capable of producing. The simplest type of such a diagram is that in which the two components A and B do not form any solid compound with each other, but separate from the solution in the pure state. This type is

illustrated by Figure 9, which shows the complete diagram for the systems composed of acetic acid (A) and benzene (B).

The freezing-point curve CD represents the composition of the solutions (S) which are in equilibrium with solid A, and the freezing-point curve DF represents the composition of the solutions which are in equilibrium with solid B at different temperatures. The point D at which the solution is in equilibrium with the two solid phases A and B is called the *eutectic point*. When a solution in the condition corresponding to this point is cooled, it solidifies completely without change
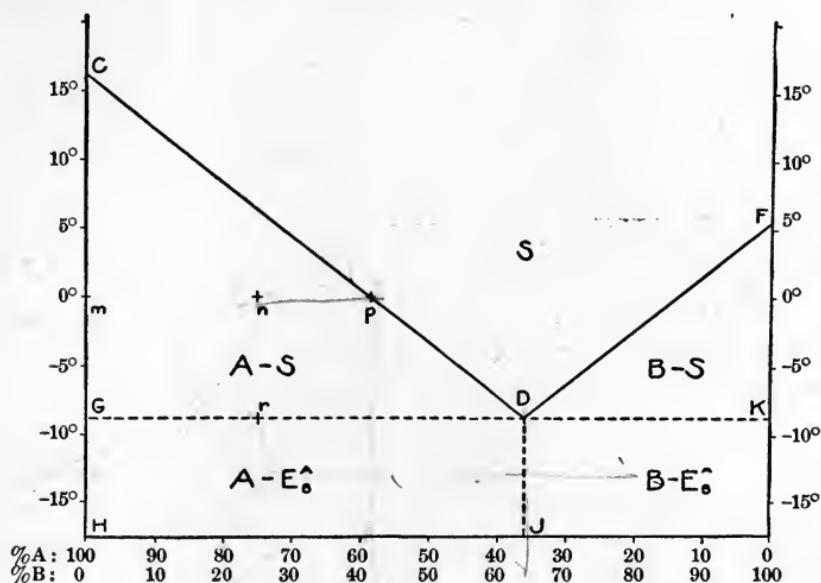
FIGURE 9

of composition or temperature to a mixture of the two solid phases A and B. This mixture is usually so fine-grained and intimate that it differs markedly in texture from ordinary mixtures of the same solid phases. It is called the *eutectic mixture*, or simply the *eutectic*.

Prob. 33. Show that the phase rule requires that a solution at the eutectic point solidify without change of temperature or composition when heat is withdrawn from it.

Prob. 34. A tube containing a solution of 80% benzene and 20% acetic acid at 10° is placed within an air jacket surrounded by a freezing mixture at —20°, so that the system slowly loses heat, till its temperature falls to —10°. Predict with the aid of Figure 9 the values of the temperature and composition of the solution at which any phase appears or disappears. State also the character of the solid mixture finally obtained.

Prob. 35.—Cooling Curves.—a. On a diagram having as ordinates the temperatures in degrees and as abscissas the time of cooling in arbitrary units draw curves representing in a general way the rate at which the temperature decreases when a solution of 80% benzene and 20% acetic acid is cooled as described in Prob. 34, assuming, first, that the liquid overcools without the separation of any solid phase; and assuming, secondly, that the solid phases separate so that there is always equilibrium. (Take into account the fact that on cooling a system there is always an evolution of heat whenever a new phase separates.) *b.* Draw on the same diagram, at the right of these curves, a new cooling curve showing how the temperature changes when pure benzene is cooled from 10° to —10°. *c.* Draw a cooling curve also for the case that a solution of 64% benzene and 36% acetic acid is cooled from 10° to —10°.

The fields in the diagram are also of much significance since the composition represented by the abscissas is understood to be that of the whole system—not merely that of the liquid phase. Thus, when the system consists of the substances in such a proportion (*e. g.,* 20% of B to 80% of A) and at such a temperature (*e. g.,* 0°) that its condition is represented by a point **n** within the field CDG, the diagram shows that it consists of the two phases, solid A and solution S of the composition (corresponding to the point **p**) at which these two phases are in equilibrium at the given temperature. Similarly, when the system has such a composition and temperature that it lies within the field GDJH, it consists of solid A and the eutectic mixture E_B^A, which always has the composition corresponding to the point D. It can readily be shown, moreover, that, when the state of the system is represented by the point **n**, the weight of solid A is to the weight of the solution present as the length of the line joining **n** and **p** is to the length of the line joining **m** and **n**; and similarly, that at any point below **r** on the same ordinate with it the weight of pure A is to the weight of the eutectic mixture present as the length of the line rD is to that of the line Gr.

Prob. 36. How do the two rectangular fields at the bottom of Figure 9 differ with respect to, *a,* the phases present; *b,* the texture of the mixture?

Prob. 37. Show that the relation stated in the last sentence of the preceding text is true.

Prob. 38. Lead (which melts at 327°) and silver (which melts at 960°) form a eutectic which melts at 304°. The heat absorbed by the fusion of one atomic weight of lead is 1340 cal. Calculate the composition of the eutectic, taking into account the facts that the first part of a freezing-point curve can be located with the aid of the laws of perfect solutions, and that the molecules of metallic elements in dilute metallic

solutions are as a rule identical with their atoms. Compare the calculated composition of the eutectic with that (4.7 at. wts. Ag to 95.3 at. wts. Pb) derived from cooling curves.

Prob. 39. Describe a method based on the facts stated in Prob. 38 by which a melt containing 1 at. wt. Ag and 99 at. wts. Pb could be enriched in silver. State the extent to which the percentage of silver could be increased by the method described. (A method of this kind has, in fact, been employed by metallurgists.)

Prob. 40. Construction of Temperature-Composition Diagrams from Cooling Curves.—Figure 10 shows the cooling curves for a series of mixtures of magnesium and lead containing the atomic percentages of lead shown by the numbers at the tops of the curves. On a diagram whose coördinates are temperature and atomic percentages plot points representing the temperature at which the solidification of each mixture begins and ends. Draw in solid lines representing the freezing-point curves. Draw also dotted lines limiting the different fields (as was done in Figure 9), and letter the fields so as to show of what the system consists in each field.
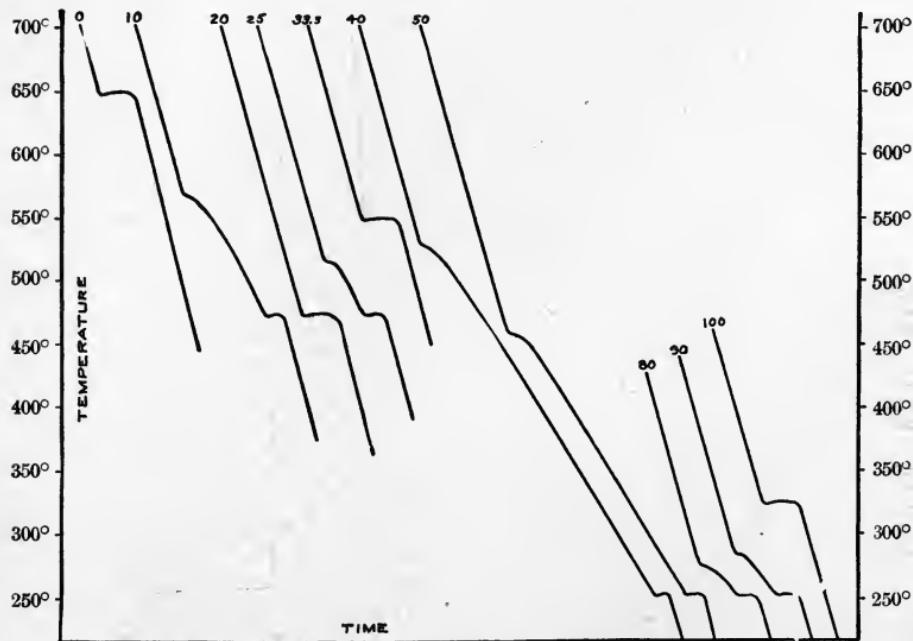
FIGURE 10

Prob. 41. Construct a temperature-composition diagram for the system composed of Na_2HPO_4 and H_2O by plotting the following values of the percentage $(100x)$ of Na_2HPO_4 in the saturated solution as abscissas against the temperature (t) as ordinates. The solid phase which is in

equilibrium with the solution (S) at a pressure of 1 atm. is indicated by the letters above the data.

	Ice	AW_{12}	AW_{12}	AW_{12}	AW_{12}	AW_7
$100x$	1.1	2.4	5.5	19.2	30.0	33.7
t	—0.5°	0°	15°	30°	35°	38°

	AW_7	AW_7	AW_2	AW_2	AW_2
$100x$	38.0	43.5	44.7	46.6	48.0
t	43°	48°	50°	55°	60°

Draw in on the diagram lines representing the equilibrium conditions, and mark each line with letters indicating the phases which coexist under the conditions represented by it.

Prob. 42. With the aid of the diagram of Prob. 40 determine all the conditions of temperature and composition at which three phases coexist, stating in each case what the three phases are.

Prob. 43. State with the aid of the diagram of Prob. 40 what changes occur in the composition of the solution, and what solid phases separate and redissolve, on cooling from 55° to —1°, at 1 atm., a solution containing, *a*, 1% Na_2HPO_4; *b*, 20% Na_2HPO_4; *c*, 46% Na_2HPO_4.

Prob. 44. What solid hydrate separates when a solution containing 15% Na_2HPO_4 is evaporated (for example, by passing a current of air through it) at 30°? at 40°? at 50°?

Prob. 45. With the aid of the diagram of Prob. 40, estimate the ratio of the solubility of $Na_2HPO_4.7H_2O$ to that of $Na_2HPO_4.12H_2O$ at 30°, expressing the solubilities in formula-weights Na_2HPO_4 per 1000 grams of water.

Prob. 46. Prove that in contact with the solution the more soluble hydrate, $Na_2HPO_4.7H_2O$, is unstable at 30° with respect to the less soluble one, $Na_2HPO_4.12H_2O$, by showing what must happen *a*, when the heptahydrate is placed in contact with a solution saturated at 30° with the dodecahydrate; *b*, when the dodecahydrate is placed in contact with a solution saturated at 30° with the heptahydrate.

Prob. 47. a. Predict from the diagram at what temperature the hydrate $Na_2HPO_4.12H_2O$ would melt if the transition into $Na_2HPO_4.7H_2O$ were avoided. *b.* Insert on the diagram dotted lines and letters showing (as in Figure 9) the significance of the different fields.

*Prob. 48.—Correlation of the Pressure-Temperature and Temperature-Composition Diagrams.—*With the aid of the diagrams of Figure 8 and of Prob. 40 make a table showing for the temperatures 20, 25, 30, 35.5, and 40° the vapor-pressures and percentage compositions of the saturated solutions and the nature of the solid phases with respect to which the solutions are saturated. (Note that the effect of pressure on the solubility is here neglected.)

Prob. 49.—Systems with Solid Phases and Two Liquid Phases.— In Figure 11 the curves CD and DE show the atomic percentages of the two liquid phases in equilibrium with each other at various temper-

atures. *a.* State all that would happen on cooling from 1000° to 300° alloys containing 40 and 90 atomic percents of zinc. *b.* State all that would happen on gradually adding zinc to molten lead at 350°, at 700°, and at 1000°.

Note.—Two liquid phases are often formed also by pairs of non-metallic substances, such as bromine and water, or phenol and water.
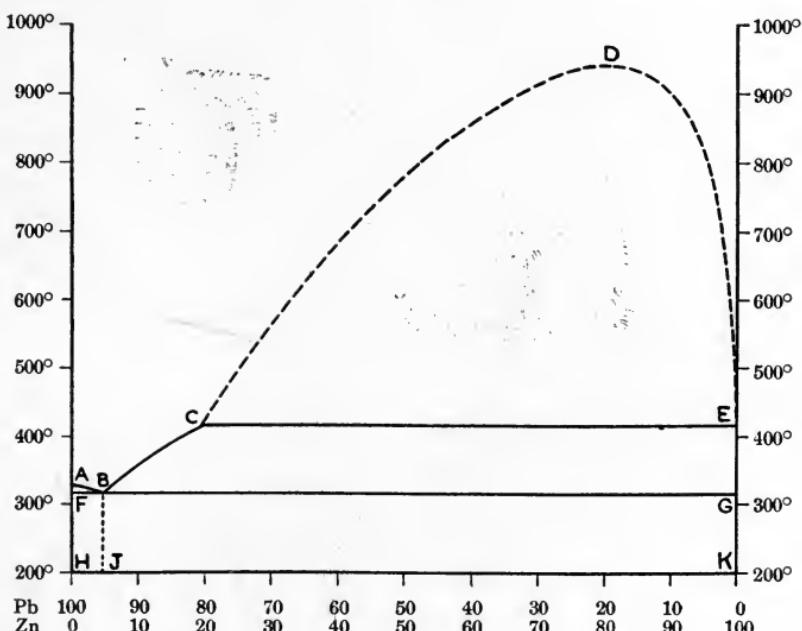

FIGURE 11

103. Systems with Liquid and Gaseous Phases.—Systems of two components having a gaseous phase and a liquid phase in which the components are miscible in all proportions have already been considered in Arts. 32 and 33. They are briefly reviewed in Prob. 50 with respect to their diagrammatic representation. The case where the two components have only limited miscibility in the liquid state was considered in Probs. 74 and 75, Art. 39.

Prob. 50. Sketch three separate diagrams corresponding to the three cases represented in the temperature-composition diagram in Figure 3, Art. 33, where the pressure on the system was fixed at 1 atm. On these sketches letter each of the fields so as to show of what phases the system consists when represented by any point on the diagram.

104. Systems involving Solid Solutions.—The components sometimes separate from the liquid solution in the form of solid solutions,

instead of in the form of the pure solid substances or of solid compounds of them. By *solid solutions* are meant physically homogeneous solid mixtures of two or more substances, that is, solid mixtures which contain no larger aggregates than the molecules of the substances. In their equilibrium relations they closely resemble liquid solutions; differing from them mainly in the respect that the equilibrium conditions are less readily established, owing to the rigidity and inertness characteristic of the solid state. Each component of a solid solution lowers the vapor-pressure of the other component according to the same principles as in the case of liquid solutions.

Prob. 51. The addition of thiophene to benzene raises the freezing-point of benzene (instead of lowering it). *a.* Show how the fact that these two substances form solid solutions with each other might account for the raising of the freezing-point, by considering the vapor-pressure relations as in Art. 34. *b.* In which solution must the mol-fraction of the thiophene be greater in order that the freezing-point may be raised?

The two components are sometimes soluble in each other in the solid state in all proportions, forming a complete series of solid solutions. In other cases each component has only a limited solubility in the other solid; so that two series of solid solutions result, each covering only a limited range of composition.

*Prob. 52.—Alloys with Complete Series of Solid Solutions.—*The cooling curves show that on cooling molten mixtures of nickel and copper solidification begins and becomes complete at the following temperatures, a solid solution separating in each case:

Percentage of nickel	0	10	40	70	100
Solidification begins	1083°	1140°	1270°	1375°	1452°
Solidification ends	1083°	1100°	1185°	1310°	1452°

a. Draw on a composition-temperature diagram two continuous curves corresponding to these data. Letter each field so as to show of what the system consists at any point within it. *b.* State what happens on slowly cooling a 50% mixture from 1400° to 1200°, giving the compositions of the liquid and solid solutions in equilibrium with each other at the temperatures at which solidification begins and ends, and at 1275°.

*Note.—*It will be seen that the melting-point–composition curves of the preceding problem are entirely similar to the boiling-point–composition curves marked I in Figure 3, Art. 33. Melting-point–composition curves are also met with analogous to the curves marked II and III in that figure, in which the broken lines now represent the composition of the liquid phase and the continuous lines the composition of the solid solution in equilibrium with it.

Prob. 53. Gold and copper form a complete series of solid solutions. One of the mixtures containing 60 atomic percent gold has a constant melting-point of 880°. Gold melts at 1063°, and copper at 1083°. *a.* Sketch the temperature-composition diagram, as in Prob. 52*a.* *b.* What indication does the diagram afford of the existence of a compound of gold and copper?

Prob. 54.—Alloys with Limited Series of Solid Solutions.—In Figure 12, the diagram for silver-magnesium alloys, in which the composition is expressed in atomic percentages, the curves KD, DL, and MF
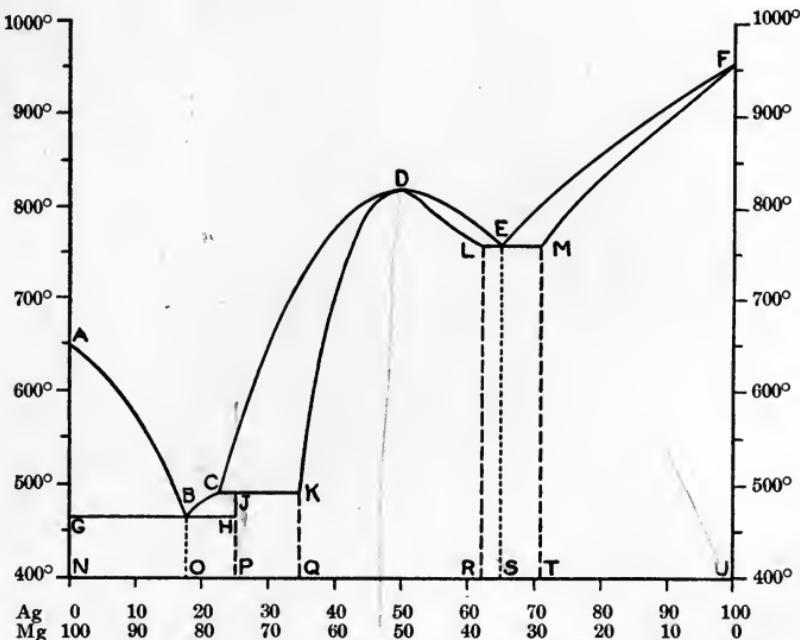
FIGURE 12

represent the composition of solid solutions in equilibrium with the liquid solutions whose composition is represented by the curves CD, DE, and EF, respectively. *a.* State what equilibria are represented by each of the other curves on the diagram and by the lines GH, CK, and LM. *b.* State what compounds are indicated by the diagram. *c—h.* State what happens on cooling slowly till complete solidification results a liquid mixture containing the following atomic percentages of silver: *c,* 90; *d,* 70; *e,* 55; *f,* 50; *g,* 25; *h,* 20. *i.* Specify the phases in which the system exists when its composition and temperature are represented by any point in each of the fields CKD, DLE, EMF, QKDLR, RLMT, and BCJH.

105. Systems with Gaseous, Liquid, and Solid Phases. Temperature-Composition Diagrams.

Applications of the Phase Rule.—

Prob. 55. a. Discuss with reference to the phase rule the effect of temperature and of pressure on the solubility of calcium carbonate in water saturated with carbon dioxide gas. *b.* Derive from the equilibrium laws applicable to dilute solutions a quantitative expression showing how the solubility of calcium carbonate varies with the pressure of the carbon dioxide gas.

Prob. 56. Silver chloride forms with ammonia two solid compounds $AgCl.1\frac{1}{2}NH_3$ and $AgCl.3NH_3$. *a.* Show by the phase rule under what conditions **AgCl** exists in contact with an aqueous solution and its vapor at 25°; *b*, under what conditions **AgCl** and $AgCl.1\frac{1}{2}NH_3$ so exist; *c*, under what conditions **AgCl**, $AgCl.1\frac{1}{2}NH_3$, and $AgCl.3NH_3$ so exist. *d.* At 25° ammonia vapor is in equilibrium with the solids **AgCl** and $AgCl.1\frac{1}{2}NH_3$ at 10 mm. and with the solids $AgCl.1\frac{1}{2}NH_3$ and $AgCl.3NH_3$ at 105 mm. Show quantitatively from these data under what conditions each of these two pairs of compounds would exist in equilibrium with an aqueous solution. *e.* Referring to the data of Prob. 35, Art. 27, what can be said as to the concentration of the aqueous solution at which **AgCl** is converted into $AgCl.1\frac{1}{2}NH_3$. *f.* Assuming that the **AgCl** in the solution is substantially all in the form of completely ionized $Ag(NH_3)_2^+Cl^-$, derive from the equilibrium laws of dilute solutions a relation between the solubility *s* of silver chloride and the partial pressure *p* of NH_3 in the vapor, first, when the solid phase is **AgCl**, and secondly, when it is $AgCl.1\frac{1}{2}NH_3$.

It will be seen from the preceding problems that the phase rule shows that the solubility at any definite temperature is some function of the pressure, and that the equilibrium laws of dilute solution (the distribution-law and mass-action law) show what that function is, provided the molecular forms in which the components exist in the solution are known. This is a characteristic difference: the phase rule is qualitative, and its application presupposes no special knowledge beyond that of the number of components and phases, and it is applicable without any limitation. The mass-action law is quantitative, its application presupposes knowledge of the molecular species present, and, if numerical values are to be computed, also of their dissociation-constants; and it is applicable in exact form only to solutions or gases at small concentrations.

The most common method of plotting the composition of three-component systems, which has the advantage of treating the three components symmetrically, is to make use of a diagram consisting of an equilateral triangle, along the three sides of which are plotted the percentages or mol-fractions of the three components, as illustrated in Figure 13. In such a diagram the vertices then represent
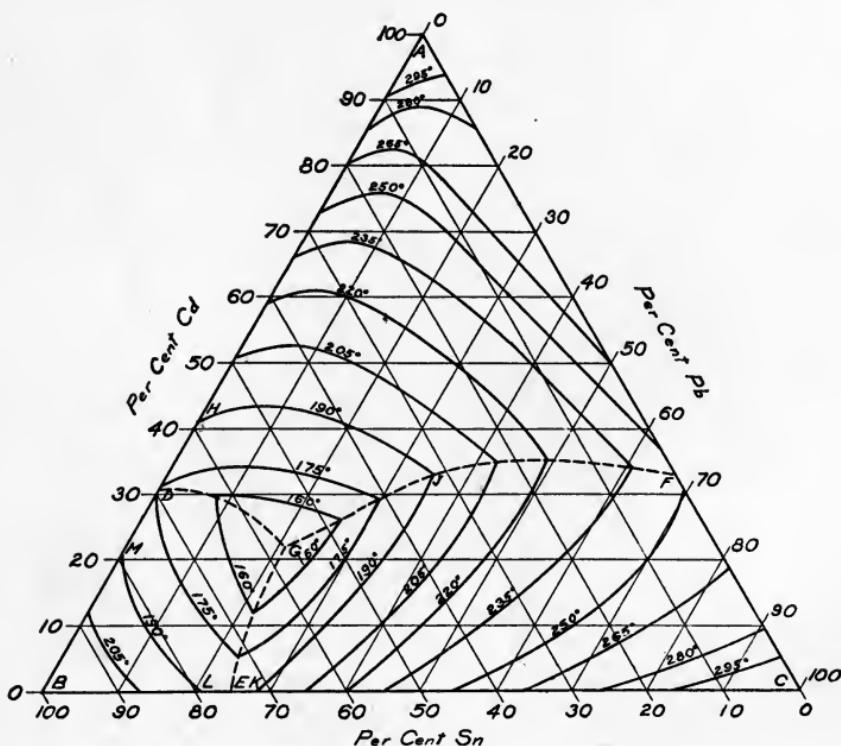

FIGURE 13

the pure components, points on the sides represent mixtures of each pair of components, and points within the triangle represent mixtures of all three components. Thus the upper vertex would represent pure cadmium; the point H, a mixture consisting of 42(atomic)% Cd and 58% Sn; and the point G, a mixture consisting of 22% Cd, 57% Sn, and 21% Pb.

At any one temperature the various compositions of the liquid phase with which any definite solid phase is in equilibrium are represented on such a diagram by a line. Thus in Figure 13 the lines HJ, JK, and LM represent at 190° the compositions of the liquid

with which solid cadmium, solid tin, and solid lead, respectively, are in equilibrium. The point J then evidently represents the composition of the liquid with which the two solid phases **Cd** and **Pb** are in equilibrium at 190°. Similar lines can be drawn corresponding to various other temperatures, thus giving a series of isotherms representing the effect of temperature on the equilibrium of the phases. The dotted line FG evidently shows the variation with the temperature of the composition of the liquid phase in equilibrium with the two solid phases **Cd** and **Pb**; the line DG shows the same thing for the two solid phases **Cd** and **Sn**; and the line EG for the two solid phases **Sn** and **Pb**. And the point G shows the only temperature and liquid composition at which the three solid phases **Cd, Pb,** and **Sn** coexist in equilibrium with the liquid phase. The mixture of three solid phases separating at this point is called the *ternary eutectic,* and the point itself the *ternary eutectic point.*

A more complete representation of the effect of temperature is secured by plotting temperatures along an axis perpendicular to the plane of the composition triangle. A prismatic model thus results, whose horizontal sections are the isotherms represented in a plane triangular diagram, like that in Figure 13.

Prob. 57. A completely liquid mixture of 50 (atomic) % Cd, 30% Sn, and 20% Pb is cooled till it wholly solidifies. *a.* State the temperature at which solidification begins and the nature of the solid phase which then separates. *b.* State the direction on the diagram which on further cooling the changing composition of the liquid phase follows. (Note that the separation of the solid phase does not change the ratio of the atomic quantities of the other two components in the liquid phase.) *c.* State the temperature at which a second solid phase begins to separate, the composition of the liquid phase, and the nature of the solid phase. *d.* Describe what happens on further cooling. *e.* Describe the texture of the solid alloy.

CHAPTER VIII

THERMOCHEMISTRY: THE PRODUCTION OF HEAT BY CHEMICAL CHANGES

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106. Introduction.—This chapter is devoted to a consideration of the heat-effects that attend changes in the physical state or chemical composition of substances. The branch of chemistry treating of these heat-effects is called *thermochemistry*. The chapter is divided into two main parts. The first part, entitled *the fundamental principles of thermochemistry,* is devoted to the energy principles underlying the subject and to the general methods of determining and expressing thermochemical quantities. The second part, entitled *the results of thermochemistry,* is devoted to the generalizations that have been derived from the results of thermochemical measurements in the case of substances in the different physical states.

107. The Law of the Conservation of Energy, or the First Law of Energetics.—The essential idea involved in the concept of *energy* is the constancy of a quantity which is involved in all the changes taking place in the universe; and this is often explicitly expressed by the statement that energy is neither created nor destroyed in any process whatever. This statement is called the *Law of the Conservation of Energy,* or the *First Law of Energetics.*

The law may be stated more concretely as follows: When a quantity of energy disappears at any place, a precisely equal quantity of energy simultaneously appears at some other place or places; and when a quantity of energy disappears in any form, a precisely equal quantity of energy simultaneously appears in some other form or forms; equal quantities of energy of different forms being understood to be such quantities as produce the same effect (for example, in modifying motion or raising temperature) when converted into the same form.

The exactness of this law has been established by many careful quantitative investigations made for the purpose. The law is also

confirmed by the correspondence of the conclusions drawn from it with well-established facts and principles. Among these may be mentioned as especially important the following principle, which is a conclusion based upon the failure of many attempts to produce a contrary result: The production of an unlimited amount of work by a machine or arrangement of matter which receives no energy from the surroundings is an impossibility. An ideal process like that here stated to be impossible is sometimes called *perpetual motion of the first kind* (to distinguish it from another kind of perpetual motion which will be described in the next chapter).

108. Energy-Changes in the Surroundings attending Changes in the State of a System.—The composition of matter under consideration is termed the *system*. A system is said to be in a definite *state* when the temperature, pressure, state of aggregation, quantity, and chemical composition of each of its parts is fixed; and a change in any of these conditions is called a *change in state.*

It follows from the First Law that, when the state of a system is fixed, its energy-content U is also fixed; and therefore also that any change in the state of a system is attended by a definite change ΔU in its energy-content (equal to the difference $U_2 - U_1$ between its energy-content in the two states), whatever be the process by which the change takes place. This corollary from the First Law of Energetics, stating that the change in the energy-content of a system is determined solely by its initial and final states, is of so much importance in thermochemical considerations that it has received a special name—the *law of initial and final states.*

Corresponding to the change in the energy-content of the *system,* there must, of course, be an energy effect in the *surroundings.* The energy lost or gained by the system may appear or disappear in the surroundings in any of its various forms; but in energetic considerations it is primarily important only to differentiate the production of *heat* from that of the other forms of energy. Such other forms of energy (that may be associated with matter) are collectively designated *work.* Under this term are included, for example, production of motion in a body, displacement of a force through a distance, change of volume under pressure, development of electrical energy, and production of chemical changes. All these forms of work are quanti-

tatively transformable into one another; but the transformation of heat into work is subject to certain limitations, which will be considered later. It is for this reason that heat and work are differentiated from each other. It will be noted that the term work is here used in a sense different from that in which it is used in the science of mechanics.

The various units in which energy-quantities are expressed and the relations between them were defined in Art. 22.

Prob. 1. When 12 g. of carbon are burned at 20° within a closed vessel (so that no work is produced) with oxygen forming carbon dioxide, 97,000 cal. are evolved; and when 28 g. of carbon monoxide are so burned with oxygen, 67,700 cal. are evolved. Show by the law of initial and final states how the heat evolved by the burning of 12 g. of carbon to carbon monoxide can be calculated.

Prob. 2. When 1 g. of liquid water is vaporized at 100° and 1 atm., the heat withdrawn from the surroundings is 537 cal., and the work produced by the expansion against the constant pressure of 1 atm. is 168 joules. At 100° and 1 atm. which has the greater energy-content, 1 g. of liquid water or 1 g. of water-vapor, and what is the difference between the two energy-contents in calories?

With the aid of the concepts of energy-content, heat, and work, the First Law may now be expressed by the statement that the increase ΔU in the energy-content of the system is equal to the heat Q withdrawn from the surroundings diminished by the work W produced in the surroundings; that is,

$$U_2 - U_1 = \Delta U = Q - W.$$

It is to be noted that Q always represents the heat *withdrawn* from the surroundings, and W the work *produced* in them; and that therefore, when actually heat is produced in the surroundings or work is withdrawn from them, the numerical value of Q or W is negative.

Thermochemistry deals with the heat-effects Q and the changes in energy-content ΔU which attend changes in the state of systems. Of these two quantities the change in energy-content is more fundamental, since it has a definite value for any definite change in state; while the heat-effect varies with the quantity of work which may be produced, and therefore with the process by which the change in state takes place, for example, whether it takes place in a closed vessel, or under the pressure of the atmosphere, or in a voltaic cell. In thermo-

chemical considerations, however, the only form of work commonly involved is that corresponding to a change in volume of the system under a constant pressure. This is considered in Art. 109.

Prob. 3. *a.* What is the system considered in Prob. 2? *b.* What is the change in state? (In describing the "change in state" the initial and final states should always be explicitly stated.) *c.* What is the value of ΔU for this change in state? *d.* What is the process by which the change in state takes place? *e.* What are the values of Q and of W for this process? *f.* By what other process (involving the production of no work) could the same change in state be brought about? *g.* What would be the values of ΔU and of Q in this case?

109. Work attending Changes in Volume.—The work produced when a system changes its volume is most readily derived for the case that the volume undergoes a change in dimensions in one direction only. Suppose that a liquid or gaseous substance contained in a cylinder is enclosed by a movable piston of cross-section a, and that a force f is exerted upon this piston, for example, by a weight placed upon it, just sufficient to compensate the expansive force of the body and prevent its expansion. Suppose now that the external force be reduced by an infinitesimal amount and that the piston rises through a distance dl. The increase of volume dv is then $a\,dl$, and the expansive force acting upon the unit of surface, which force is called pressure p, is f/a. The work dW produced by the expansion is therefore given by the equations:

$$dW = f\,dl = p\,a\,dl = p\,dv.$$

That is, the work is equal to the product of the pressure into the infinitesimal increase of volume that takes place. It can be easily demonstrated that this equation also holds true in the general case in which the volume increases in dimensions in any number of directions.

The general expression for the work produced when a body undergoes a change of volume from v_1 to v_2, is therefore:

$$W = \int_{v_1}^{v_2} p\,dv.$$

It is evidently necessary to know the functional relation between pressure and volume before the integration can be carried out.

When the pressure is constant during the change of volume, the equation evidently becomes:

$$W = p \ (v_2 - v_1).$$

Prob. 4. Calculate the work in ergs and in calories produced by the vaporization of one formula-weight of water at 100° against the pressure of 1 atm. The specific volume of liquid water at 100° is 1.043, and that of saturated water-vapor at 100° is 1650.

Prob. 5. a. Formulate an exact expression (in terms of the volumes involved) for the work produced when N mols of hydrogen are produced by dissolving an equivalent quantity of zinc in dilute sulphuric acid solution at $T°$ at a constant pressure p. *b.* Simplify this expression by neglecting the relatively small volumes involved and by applying the perfect-gas law. *c.* Calculate the work in ergs and calories produced when 1.008 grams of hydrogen are produced at 20°.

Prob. 6. Calculate the work in calories produced when the reaction $CO + \frac{1}{2}O_2 = CO_2$ takes place at 20° and 1 atm.

Prob. 7. a. Show that, in general, when any change in state which takes place at constant temperature and pressure is attended by an increase ΔN in the number of mols of the gaseous substances present, the work produced in the surroundings is given approximately by the expression $W = \Delta N \ R \ T$. *b.* Give the value of ΔN in this expression for the change of state involved in each of the three preceding problems.

Prob. 8. Calculate the work in calories produced when 1 mol of oxygen at pressure p and temperature T is heated at constant pressure through one degree.

110. Heat-Effects attending Changes in Temperature.—A comparatively simple kind of change of state is that which a system undergoes when its temperature is increased. The ratio of the quantity of heat dQ absorbed when its temperature rises from T to $T + dT$ to the rise of temperature dT is called its *heat-capacity* (C) at $T°$; that is, $C = dQ/dT$. The heat-capacity is substantially equal to the quantity of heat absorbed when the temperature rises one degree. When the heating takes place without change of pressure, the ratio dQ/dT is called the *heat-capacity at constant pressure* C_p. When the heating takes place without change of volume, the ratio is called the *heat-capacity at constant volume* C_v. The heat-capacity of any system is the sum of the heat-capacities of its homogeneous parts; and the heat-capacity of any such part is the product of its weight by the heat-capacity of one gram of it, which is called its *specific heat-capacity* $\overline{C}$. The heat-capacity of one atomic weight, one mol, or one formula-weight of a pure substance is called its *atomic, molal,* or *formal heat-capacity.*

Prob. 9. When 100 g. of silver at 100° are immersed in 1000 g. of water at 15.000° the temperature rises to 15.475°. Calculate the heat-capacity of this weight of silver and the specific and atomic heat-capacities of silver, assuming these quantities to be constant between 15° and 100°.

Prob. 10. The molal heat-capacity of oxygen at constant pressure at the temperature T is given by the expression $M \overline{C}_p = 6.50 + 0.0010T$. Calculate the heat absorbed in heating 2.24 liters of oxygen at 0° and 1 atm. to 100°, the pressure remaining constant.

111. Heat-Effects attending Changes in State at Constant Temperature.—The heat withdrawn from or imparted to the surroundings when a change takes place in the state of a system which is kept at a constant temperature is experimentally determined by calorimetric measurements, which involve the principles illustrated by the following problem.

Prob. 11. Into a calorimeter containing $50H_2O$ at 20.00° $1KCl$ at 20.00° is introduced, and the temperature falls to 15.11°. *a.* What change in state takes place in this process, considering the calorimeter to be a part of the system; and what is the change in the energy-content of the system, neglecting the small quantity of work produced and any loss of heat by radiation? *b.* What change in state takes place when $1KCl$ is dissolved in $50H_2O$ at 20°? *c.* In order to calculate the heat-effect attending this change in state, what other change in state must be combined with that occurring in the calorimeter? *d.* State what additional data would be needed to calculate this heat-effect, and formulate an expression by which the calculation could be made. *e.* Calculate the value of this heat-effect with the aid of such of the following data as may be needed: the heat-capacity of the calorimeter is 19 cal. per degree; the specific heat-capacity of solid potassium chloride is 0.166, of water is 1.00, and that of the solution of $1KCl$ in $50H_2O$ is 0.904 cal. per degree.

Changes in state at constant temperature may take place either without change of volume or without change of pressure. The different heat-effects attending these two different changes in state are known as the *heat-effect at constant volume* Q_v and the *heat-effect at constant pressure* Q_p.

The heat-effect at constant pressure is the one which is usually called the *heat of reaction*, and the one which is commonly recorded in tables of constants. There is difference of usage regarding the algebraic sign of the heat of reaction: when heat is actually evolved by the reaction, the heat of reaction is usually taken positive in thermo-chemical considerations. but negative in thermodynamic considera-

tions. In this book a uniform convention, corresponding to the thermodynamic one, is employed throughout; heat-effects being always considered positive when heat is absorbed (as in the vaporization of water) and negative when it is evolved (as in the combustion of hydrogen and oxygen).

112. Changes in Energy-Content and in Heat-Content attending Changes in State.—Having discussed the determination of the work and heat produced in the surroundings by processes involving a change in the state of a system, the corresponding change taking place in the energy-content of the system itself may be now considered. When the change in state takes place at constant volume, it is evident that no work is involved, and that therefore the heat absorbed Q_v from the surroundings is equal to the increase $U_2 - U_1$ in the energy-content of the system. When, on the other hand, the change takes place at constant pressure, there is not only a quantity of heat Q_p withdrawn from the surroundings, but also a quantity of work equal to $p(v_2 - v_1)$ produced in them. The increase $U_2 - U_1$ in the energy-content of the system is then equal to $Q_p - p(v_2 - v_1)$. The change in energy-content may thus be determined for changes in state which can be made to take place either at constant volume or at constant pressure.

Instead of determining and recording the values of $U_2 - U_1$ for various changes of state, it is generally more convenient to employ the values of the quantity $(U_2 + p_2 v_2) - (U_1 + p_1 v_1)$. The quantity $U + p v$, like the quantity U, is a property of the system which always has a definite value when the system is in a definite state, and which always changes in value by a definite amount when the system changes from one state to another, whatever be the process by which the change in state is brought about; for it is evident that the pressure p and the volume v, as well as the energy-content U, have values which are determined by the state of the system. In other words, a law of initial and final states applies to the change in the quantity $U + p v$, just as it does to the change in the quantity U. For brevity, this quantity $U + p v$ will be represented by a single letter H, and will be called the *heat-content* of the system, it being understood that this term is a purely conventional one which does not imply that the energy quantity denoted by it is a heat quantity, any more than the term energy-content implies it.

For any change in state taking place by any process whatever, the change in heat-content may be found by subtracting from the heat-effect attending the process the work produced by it diminished by the increase in the pressure-volume product; that is, in general:

$$\Delta H = Q - [W - \Delta(pv)].$$

For a change in state for which the initial and final pressures p_1 and p_2 have the same value p, the increase ΔH in the heat-content is equal to the heat-effect Q_p when the change takes place at the constant pressure p; that is, it is equal to the heat of reaction commonly employed.

Prob. 12. Derive the two conclusions stated in the last two paragraphs of the preceding text.

Prob. 13. a. When the reaction $2\,CO + O_2 = 2\,CO_2$ takes place without change of temperature or pressure in a system consisting of 2 mols of CO and 1 mol of O_2 at 20° and 1 atm., the heat-effect is —136,000 cal. What is the increase in the heat-content, and what is the increase in the energy-content, of the system? *b.* When the reaction takes place in the same mixture without change of temperature or volume, the heat-effect is —135,420 cal. What is the increase in the heat-content and what is the increase in the energy-content in this case? *c.* In what respect does the final state of the system in *a* differ from that in *b*, and what conclusion can be drawn from a comparison of the results obtained in *a* and *b* as to the change in energy-content and in heat-content that would attend the change from the final state in *a* to the final state in *b*? (It will be seen later that such a conclusion is justifiable only when the system consists of a perfect gas.)

113. Expression of Heat-Effects by Thermochemical Equations.— In order to express the changes in heat-content that attend changes in state, especially those involving chemical reactions, at any constant temperature and pressure, equations are conveniently employed in which the heat-contents of the various substances involved are represented by their chemical formulas, and in which the change in heat-content is shown by placing a numerical term on the right-hand side of the equation. For example, the expression

$$\mathbf{Fe_2O_3} + 3\,CO = 2\,\mathbf{Fe} + 3\,CO_2 + 9000 \text{ cal. (at 20°)}$$
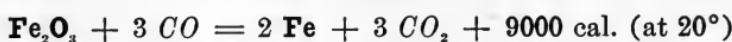
signifies that at 20° and 1 atm. (this pressure being understood unless some other pressure is stated) the heat-content of one formula-weight of ferric oxide plus that of three formula-weights of carbon monoxide

is equal to the heat-content of two formula-weights of iron plus that of three formula-weights of carbon dioxide plus 9000 cal.; 9000 cal. being the decrease $(-\Delta H)$ in the heat-content of the system, which is equivalent to the heat evolved by the system when the reaction takes place at a constant temperature and pressure. Such expressions are called *thermochemical equations,* or specifically, *heat-content equations.*

As indicated in the preceding equation, the fact that a substance is in the solid state is shown by black-face type, and the fact that it is in the gaseous state by italics. The fact that a substance is liquid is denoted by ordinary type, and the fact that a substance is dissolved in x formula-weights of water is shown by attaching the symbol xAq to the formula of the substance. Thus the equation

$$\textbf{KCl} + 100\text{Aq} = \text{KCl}100\text{Aq} - 4400 \text{ cal. (at } 20°)$$

signifies that when at 20° one formula-weight of solid potassium chloride is dissolved in 100 formula-weights of water there is an increase of 4400 cal. in the heat-content of the system, corresponding to an absorption of 4400 cal. from the surroundings. When the substance is dissolved in so large a quantity of water that the addition of more water produces no appreciable heat-effect, the symbol ∞ Aq may be attached to the formula of the substance.

These thermochemical equations can evidently be treated strictly as algebraic equations, and can be combined with one another by addition or subtraction; for every quantity in them has a definite value (namely, that of the heat-content of the substance represented by the formula), irrespective of the other quantities that occur with it in the equations.

Prob. 14. The union at 20° and 1 atm. of 1 g. of aluminum with oxygen is attended by a heat-evolution of 7010 cal.; and the union of 1 g. of carbon with oxygen to form carbon monoxide is attended by a heat-evolution of 2420 cal. Express these data in the form of thermochemical equations; and calculate from them the heat of the reaction $\textbf{Al}_2\textbf{O}_3 + 3\textbf{ C} = 2\textbf{ Al} + 3\textit{ CO}$ at 20°.

Prob. 15. a. Express the following data in the form of thermochemical equations, employing the conventions described in the preceding text: The heat of formation of 1 mol gaseous HCl from the elementary substances is —22,000 cal. Its heat of solution in 100 formula-weights of water is —17,200. The heat of the reaction between 1 mol gaseous chlorine and a solution of 2 formula-weights HI in 200 formula-weights

of water, forming solid iodine and a dilute HCl solution is —52,400 cal. The heat of solution of 1 mol gaseous HI in 100 formula-weights of water is —19,200 cal. *b.* By combining these equations calculate the heat of formation of 1 mol gaseous HI from gaseous hydrogen and solid iodine.

Although it is true that only *changes* in heat-content can be determined, yet it is convenient to employ an arbitrary scale of heat-content which has as its zero-points the heat-contents of the various elementary substances at the temperature under consideration, at a pressure of one atmosphere, and in the form which is most stable at this temperature and pressure. Under this convention the heat-content (H) of any compound substance is evidently equal to the increase in heat-content (ΔH) which attends its formation out of the elementary substances; and in any thermochemical equation the formula of a substance may evidently be replaced by the numerical value of its heat of formation. For example, the heat-content at 20° of one formula-weight of gaseous hydrogen bromide, or the numerical value of the formula 1*HBr*, is —8500 cal.; for —8500 cal. is the heat absorbed when it is formed out of gaseous hydrogen and liquid bromine at 20° and 1 atmosphere. Similarly the heat-content of a potassium chloride solution represented by the formula KCl100Aq is —101,200 cal.; for this is the sum of the heat-effect (—105,600 cal.) attending the formation of one formula-weight of solid KCl out of solid potassium and gaseous chlorine at 20° and of the heat-effect (4,400 cal.) attending its solution in 25 formula-weights of water at 20°. This example of the heat of formation of a solution, which may be expressed by the equation **K** + ½*Cl*₂ + 100Aq = KCl100Aq + 101,200 cal., shows that in thermochemical equations the symbol *x*Aq (not attached to another formula) has, like the formulas of elementary substances, the value zero; for the water represented by it has not been formed out of its elements. (Water which has been so formed is represented by the formula *x*H₂O).

It is evident that the employment of heats of formation greatly simplifies the task of determining and systematizing thermochemical data; for, instead of measuring and recording the change in heat-content attending every chemical reaction, it suffices to do this for the formation of every compound out of the corresponding elementary substances. The numerical values of the heats of formation so determined may then be substituted in any thermochemical equation, and

the change in heat-content attending the reaction expressed by it may thus be calculated.

Prob. 16. Calculate the heat-effect that attends at 20° the reaction **PbS + 2PbO = 3Pb +** SO_2, from the following heats of formation at 20°: **PbO,** —50,300 cal.; **PbS,** —19,300 cal.; SO_2, —70,200 cal.

Prob. 17. At 20° the heat of combustion of one mol of acetylene (C_2H_2) is —313,000 cal. Calculate its heat of formation. The heat of formation of $1H_2O$ is —68,400 cal., and that of $1CO_2$ from charcoal and oxygen is —96,600 cal.

Prob. 18. a. State just what heats of formation are denoted by the second and third terms in the following equation:

$$Zn + 2HCl \infty Aq = ZnCl_2 \infty Aq + H_2 + 34,200 \text{ cal. (at 20°)}.$$
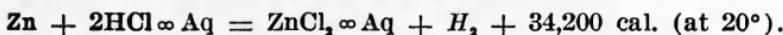
b. Write the complete thermochemical equations which express these heats of formation, taking into account the facts that the heat of formation of 1 mol of gaseous HCl is —22,000 cal. and that its heat of solution in a large quantity of water is —17,300 cal.

114. Indirect Determination of the Heat-Effects of Chemical Changes.— On account of radiation-errors the heat-effect can be directly determined by calorimetric measurements only for those chemical changes which take place completely within a few minutes, and for such changes only when the temperature is not greatly different from the room-temperature. It is, however, possible to calculate the heat-effects of many other changes from those which have been directly measured, by applying the law of initial and final states. This is illustrated for changes at the room-temperature by the problems of the preceding articles and by the following problems, which are solved by combining the proper thermochemical equations in such a way as to eliminate the heat-content of all the substances except those involved in the reaction under consideration. The method commonly employed for determining heat-effects at temperatures much higher or lower than the room-temperature is described in the next article.

Prob. 19. Calculate the heat of formation of one formula-weight of solid zinc hydroxide from the following equation and from the other necessary data, which have been given in preceding problems:

$$Zn(OH)_2 + 2HCl \infty Aq = ZnCl_2 \infty Aq + 2H_2O + 19,900 \text{ cal.}$$
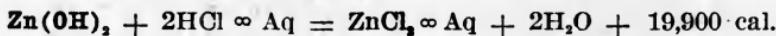
Prob. 20. Calculate the heat of formation at 20° of one formula-weight of H_2SO_4 from the following data at 20° and those given in preceding problems: the heat of solution in a large quantity of water of 1 mol gaseous SO_2 is —8000 cal., and that of 1 formula-weight H_2SO_4 is —18,000 cal. One mol gaseous Cl_2 acting on a dilute solution of 1 mol

SO_2 with formation of a dilute solution of HCl and H_2SO_4 produces a heat-evolution of 73,900 cal. (Note that when x formula-weights of H_2O are involved in the chemical reaction the symbol xH_2O must appear in the thermochemical equation, even though ∞ Aq may also occur in it.)

Prob. 21. A direct determination of the heat-effect of the reaction $CH_3CH_2OH \infty Aq + O_2 = CH_3CO_2H \infty Aq + H_2O$ is not practicable. State what measurements could be made which would enable this heat-effect to be calculated; and show how it would be calculated from the results of such measurements.

Prob. 22. Suggest a series of chemical reactions from whose heat-effects, which must be readily determinable in a calorimeter, the heat of formation of $Na_2CO_3.10H_2O$ at 20° could be calculated. Write the thermochemical equations, and indicate how they would be combined to yield the desired result.

Prob. 23. Calculate the heat-effects of the following reactions at room-temperature, referring to Landolt-Börnstein Tabellen for the heats of formation, of combustion, and of solution needed:

   a. $H_2S + 2Ag = Ag_2S + H_2$.

   b. $C_6H_{12}O_6$ (glucose) $= 2C_2H_5OH + 2CO_2$.

   c. $Zn + CuSO_4 400Aq = Cu + ZnSO_4 400Aq$.

115. Influence of Temperature on the Heat-Effects attending Chemical Changes.—The heat-effect at constant pressure of a chemical change taking place at any temperature can be derived from the heat-effect at constant pressure at any other temperature by the following consideration of two different processes resulting in the same change in state. In one process cause the chemical change (for example, the union of 1 mol of CO with $\frac{1}{2}$ mol O_2) to take place at a pressure p and temperature T_1, and heat the products (the carbon dioxide) under the pressure p to the other temperature T_2; and, in the second process, heat the reacting substances (the carbon monoxide and oxygen) under the pressure p from T_1 to T_2, and cause them to combine (forming carbon dioxide) at the pressure p and the temperature T_2. Since in each of these processes the system changes from the same initial state (1 mol of CO and $\frac{1}{2}$ mol O_2 at p and T_1) to the same final state (1 mol CO_2 at p and T_2), the total change in heat-content must be the same in the two processes; and therefore the heat-effect at constant pressure p and temperature T_2 must differ from the heat-effect at constant pressure p and temperature T_1 by the same amount as the heat absorbed in heating the reaction-products differs from that absorbed in heating the reacting substances from T_1 to T_2 at the constant pressure p.

Prob. 24. Demonstrate the truth of the principle stated in the preceding paragraph by considering the increase in heat-content attending each step of the processes there described.

Prob. 25. Calculate the heat of formation of one formula-weight of PbO at 200° from its heat of formation (—50,300 cal.) at 20° and from the mean specific heat-capacities at constant pressure of lead (0.032), of oxygen (0.212), and of lead oxide (0.052).

Prob. 26. Calculate the heat of formation of 1 mol gaseous water at 1000° from the following data. The heat of formation of 1 mol liquid water at 20° is —68,400 cal. Its heat of vaporization at 100° is 9670 cal. The molal heat-capacity at constant pressure at T is $6.50 + 0.0010\,T$ for hydrogen or oxygen, and $8.81 - 0.0019T + 0.000,002,22T^2$ for water.

Prob. 27. Calculate the heat of the reaction $K\,(\text{liquid}) + \tfrac{1}{2}Cl_2 = KCl$ at 160°, referring to Landolt-Börnstein Tabellen for the necessary data.

Prob. 28. *a.* State what quantity is equivalent to the change per degree of the heat-effect of a reaction at constant pressure. *b.* Formulate an integral which is a general expression for the difference in the heat-effects Q_2 and Q_1 of any reaction at two temperatures T_2 and T_1, when no change takes place in the state of aggregation between those temperatures.

THE RESULTS OF THERMOCHEMISTRY

116. Constancy of the Heat-Content of Perfect Gases at Constant Temperature.—Experiments have shown that when a perfect gas expands at a constant temperature without producing any work (for example, when it expands within a calorimeter from one vessel into another vessel previously evacuated), there is no heat-effect in the surroundings (no change of temperature in the calorimeter). Such experiments have established the important law that the energy-content U of a definite quantity of a perfect gas at any definite temperature has the same value, whatever be its volume and pressure; in other words, that $\Delta U = 0$ when a perfect gas changes its volume and pressure at a constant temperature.

The same principle is evidently true of the heat-content H of a perfect gas; for this is by definition equal to $U + p\,v$, and $p\,v$ does not change in value when a perfect gas changes its volume and pressure. Therefore, $\Delta H = 0$ when a perfect gas changes its volume and pressure at a constant temperature.

The law that the energy-content of a perfect gas at a constant temperature is independent of the volume leads to the conclusion that, when the expansion of a perfect gas at a constant temperature is attended by the production of work, there must be a quantity of heat absorbed by it equal to the work produced; for it follows from the equation $\Delta U = Q - W$ that $Q = W$ when $\Delta U = 0$.

In the case of actual gases there are small deviations from these principles at moderate pressures, and large deviations at high pressures, in the direction corresponding to an increase in energy-content with increase of volume. This increase is most accurately determined by experiments, like that described in the following problem, in which the gas is caused to expand without producing work (except that equivalent to the change in its pressure-volume product) and without taking up heat from the surroundings. It undergoes thereby a decrease in temperature, which is often called from its discoverers the *Joule-Thomson Effect*. From this decrease in temperature and from heat-capacity data the quantity of heat which must be imparted to the gas to heat it in its expanded state to its original temperature is then calculated.

Prob. 29.—Determination of the Change in Heat-Content by Porous-Plug Experiments.—Carbon dioxide at pressure p_1 (*e. g.*, 2 atm.) and temperature T_1 (*e. g.*, 20.00°) is caused to flow continuously through a well-insulated hardwood tube containing a porous plug of cotton. On passing through the plug its pressure falls to p_2 (*e. g.*, 1 atm.), and it emerges from the tube at this pressure. After the gas has flowed so long that every part of the apparatus has assumed the temperature of the gas in contact with it, the expansion of the gas takes place without exchange of heat with the surroundings. · Its temperature after passing through the plug is found to be T_2 (*e. g.*, 18.86°). *a.* What other process must be combined with this one in order that the net result of the two processes may be the expansion of one mol of the gas from volume v_1 to volume v_2 at a constant temperature T_1? *b.* Formulate expressions for the work produced W, the heat absorbed Q, the change in energy-content ΔU, and the change in heat-content ΔH for each of these two processes. (Note that in the first process a volume v_1 of the gas disappears on one side of the plug under a constant pressure p_1, and that a certain volume v_2' of the gas is produced on the other side of the plug under a constant pressure p_2.) *c.* Combine these results so as to give an expression for the change in energy-content and the change in heat-content that attends a change in volume from v_1 to v_2 of one mol of the gas at a constant temperature T_1. *d.* Calculate in calories the change in energy-content and the change in heat-content attending the expansion of 1 mol of carbon dioxide from a pressure of 2 atm. to a pressure of 1 atm. at 20°. Use the following data in addition to those given above : the molal volume of carbon dioxide at 20° and 2 atm. is 11,890 ccm., and at 20° and 1 atm. is 23,920 ccm. ; its molal heat-capacity at 20° and at a constant pressure of 1 atm. is 8.92 cal. per degree.

Note.—The decreases in temperature that have been observed in similar experiments with carbon dioxide at a series of temperatures are : 1.35° at *0°*, 1.14° at *20°*, 0.83° at *60°*, and 0.62° at *100°* ; and that observed with air, a more nearly perfect gas, is 0.25 at *20°*. It will be noted that this last value signifies that, when a quantity of air expands at 20° from a pressure of 2 atm. to one of 1 atm., the increase in its heat-content is equal to the increase in its heat-content which takes place when it is heated at constant pressure through 0.25°. This gives a general idea of the magnitude of the effect under consideration.

117. The Heat-Capacity of Perfect Gases in Relation to Pressure and Volume.

—From the law that the heat-content of a perfect gas at a definite temperature does not vary with changes in its pressure and volume, the following principles can be derived : the heat-capacity of a perfect gas both at constant pressure and at constant volume at a definite temperature has the same value whatever be the pressure and

volume; and the molal heat-capacity of a perfect gas at constant pressure is greater than that at constant volume by an amount equal in value to the gas-constant R, whatever be the gas and whatever be the temperature.

Prob. 30. Derive the first principle stated in the preceding text by considering that a perfect gas changes by two different processes from a volume v_1 at pressure p_1 and temperature T_1 to a volume v_2 at pressure p_2 and temperature T_2.

Prob. 31. Derive the second principle stated in the preceding text by a consideration similar to that employed in the last problem.

118. The Heat-Capacity of Perfect Gases in Relation to Composition and Temperature.— The molal heat-capacity of gases at constant volume depends primarily on the complexity of the molecules of the gas. It has the smallest value for gases with monatomic molecules, such as mercury and helium; and it has the same value, namely $\frac{3}{2}R$ or 2.98 calories per degree, for all such gases at all temperatures. It has a considerably larger value for gases with diatomic molecules— a value which is approximately the same for nearly all such gases, namely, for H_2, O_2, N_2, NO, CO, HCl, HBr, and HI, and one which varies appreciably, but not very greatly, with the temperature. Its value for these gases at any temperature T is given by the expression $M\overline{C}_v = 4.50 + 0.0010T$. The corresponding expressions for the molal heat-capacity of perfect gases at constant pressure, which has been seen to be always greater than that at constant volume by the gas-constant R, are $M\overline{C}_p = 4.97$ for monatomic gases, and $M\overline{C}_p = 6.50 + 0.0010\,T$ for most of the diatomic gases. A few diatomic gases, namely, Cl_2, Br_2, I_2, and ICl, have at room-temperature larger values of the heat-capacity than do the other diatomic gases, and the values increase more rapidly with the temperature; thus, though these heat-capacities have not been satisfactorily determined, the incomplete data that exist may be expressed roughly by the equation $M\overline{C}_p = 6.5 + 0.004\,T$. The only general statement that can be made in regard to the heat-capacities of triatomic and other polyatomic gases is that the values are much larger than those for the diatomic gases and that they increase with the complexity of the molecule; thus the value of $M\overline{C}_p$ at 100° is 6.9 for N_2 and O_2, 8.3 for H_2O and H_2S, 9.4–9.9 for CO_2, SO_2, and N_2O, 9.0 for NH_3, 21 for alcohol (C_2H_6O), and 34 for ether

($C_4H_{10}O$). In the case of these polyatomic gases the increase of the heat-capacity with the temperature has to be expressed by quadratic or cubic functions; thus in the case of carbon dioxide and sulphur dioxide, $M\overline{C}_p = 7.0 + 0.0071T - 0.00,000,186T^2$. The heat-capacity of water-vapor can be expressed by a similar function (see Prob. 26).

Prob. 32.—Determination of the Complexity of the Molecules of a Gas from the Heat-Capacity-Ratio.—From the experimentally determined velocity of sound in a gas the heat-capacity-ratio C_p/C_v can be calculated. This ratio has been thus found to be 1.67 in the case of argon. *a.* Compare this value with the values of the ratio calculated for a monatomic gas and for a diatomic gas at 20° with the aid of the statements made in the preceding text. *b.* Show how the atomic weight of argon can be obtained by combining this result with the value of another experimentally determined property of the gas.

119. Heat-Effects at Constant Pressure and at Constant Volume attending Reactions involving Perfect Gases.—The law that the heat-content of a perfect gas at a definite temperature is independent of its pressure leads to the conclusion that in the case of reactions involving gases at small pressures the heat-effect Q_p at constant pressure is greater than the heat-effect Q_v at constant volume by an amount approximately equal to the work W produced when the reaction takes place at constant pressure. This work has already been shown to be approximately equal to $\Delta N\,R\,T$, where ΔN denotes the increase in the number of mols of the gaseous substances present. The derivation and application of this principle are illustrated by the following problems.

Prob. 33. Show that $-R\,T$ is the difference between the quantities of heat absorbed when at $T°$ a mixture of 2 mols of CO and 1 mol of O_2 at 1 atm. unites to form CO_2 in one case at constant pressure (for example, in an open calorimeter) ; and in another case at constant volume (for example, in a bomb calorimeter). Note that the change of state which results when the reaction takes place at a constant pressure of 1 atm. could also be brought about by a process consisting of two steps, namely, by causing the mixture of CO and O_2 at 1 atm. to change at constant volume to CO_2 (whereby the pressure would become $\frac{2}{3}$ atm.), and then compressing it till its pressure becomes 1 atm.

Prob. 34. When 1 mol of naphthalene ($C_{10}H_8$) is burnt with oxygen at 20° in a bomb-calorimeter 123,460 cal. are evolved. Calculate its heat of combustion at constant pressure.

120. The Heat-Capacity of Solid Substances.—Experiments have shown that the atomic heat-capacity of all solid elementary substances is relatively small at temperatures below —100°, that with rising temperature it increases at different rates in the case of different substances, and that, after room-temperature is reached, it increases as a rule only slowly with further increase of temperature. At room-temperature the atomic heat-capacity has approximately the same value in the case of all elements with atomic weights above 35, and in the case of the metallic elements of still lower atomic weight. The average value at room-temperature is 6.2 calories per degree. Deviations of ± 0.4 unit are not uncommon; and deviations of $+0.7$ to $+0.9$ unit are exhibited by some elements (for example, by sodium, potassium, and iodine) which at room-temperature are not much below their melting-points. In the case of the non-metallic elements with smaller atomic weights than 35 the atomic heat-capacity has a value much smaller than 6.2 at room-temperature; thus the value for boron is 2.6, for graphite 1.9, for silicon 4.8, for phosphorus 5.6, and for sulphur 5.5. This principle in regard to the approximate constancy of the atomic heat-capacities of solid elementary substances is known as the *law of Dulong and Petit.*

The following table. which contains experimentally determined values of the atomic heat-capacity, illustrates the preceding statements:

Element	At. Wt.	—200°	—100°	—50°	0°	50°	100°	200°	300°
Aluminum	27.1	2.0	4.6	5.3	5.6	5.8	6.0	6.3	6.7
Antimony	120.2	4.2	5.4	5.7	5.9	6.0	6.1	6.2	6.3
Cadmium	112.4	4.3	5.8	6.1	6.2	6.2	6.3	6.8	9.4
Chromium	52.0	2.0	4.1	4.9	5.4	5.7	5.8	6.1	6.4
Copper	63.6	3.3	5.0	5.5	5.8	5.9	6.0	6.1	6.2
Iron	55.8	3.0	4.6	5.2	5.8	6.2	6.6	7.0	7.4
Lead	207.1	5.6	5.9	6.0	6.2	6.3	6.5	6.7	7.0
Magnesium	24.3	3.5	4.9	5.4	5.8	6.0	6.2	6.9	7.7
Silver	107.9	4.0	5.6	6.0	6.3	6.5	6.6	6.9	7.1
Sodium	23.0	5.1	5.9	6.3	6.7	7.1	7.5	..	..
Boron	11.0	..	1.6	2.0	2.4	2.8	3.2	4.0	..
Diamond	12.0	0.1	0.5	0.8	1.1	1.6	2.3	3.2	3.9
Sulphur	32.1	2.5	4.3	4.9	5.3	5.6	5.8	..	..

The law of Dulong and Petit, even though it is only an approximate principle, may evidently be employed for determining what multiple of the combining weight of an element is its atomic weight;

and the application of this law was in fact one of the most important methods by which the present system of atomic-weight values was originally established.

A simple principle has also been discovered in regard to the formal heat-capacity of solid compound substances at room-temperature. It has been found, namely, that this property is approximately an additive one, that is, one whose value can be approximately calculated by adding together certain values representing the heat-capacity of the elements contained in the compound. This principle is expressed by the following equation, which shows at the same time the values of the constants (the so-called atomic heat-capacities) for all the common elements:

$$M\overline{C}_p = 6.2\ n_E + 4.0\ n_O + 2.3\ n_H + 1.8\ n_C + 5.4\ n_S + 2.7\ n_B + 5.4\ n_P + 3.8\ n_{Si}.$$

In this equation $M\overline{C}_p$ represents the formal heat-capacity of the compound at constant pressure at room-temperature; n_O, n_H, n_C, n_S n_B, n_P, and n_{Si} are the number of atomic weights of oxygen, hydrogen, carbon, sulphur, boron, phosphorus, and silicon present in one formula-weight of the compound; and n_E is the number of atomic weights of any other element so present. The values given for the constants are average values derived from heat-capacity measurements with solid compounds.

The following table illustrates the degree of correspondence which exists between the values of the formal heat-capacity so calculated and those measured experimentally:

Substance	Calc.	Meas.	Substance	Calc.	Meas.
H_2O (ice)	8.6	9.7	PbN_2O_6	42.6	38.8
Al_2O_3	24.4	20.5	$CaSiO_3$	22.0	21.3
Fe_2O_3	24.4	25.6	$K_4Fe(CN)_6$	79.0	78.8
Sb_2S_3	28.6	28.7	$CuSO_4.5H_2O$	70.6	67.2
KCl	12.4	12.4	$AlK(SO_4)_2.12H_2O$	158.	165.
$PbCl_2$	18.6	18.5	$C_{10}H_8$	36.	40.
$CaCO_3$	20.0	20.2	$H_2C_2O_4$	24.2	25.1

It will be observed that differences of ten percent between the calculated and measured values are not uncommon.

Prob. 35. Calculate an approximate value at 20° of the specific heat-capacity at constant pressure of *a*, platinum; *b*, silver bromide; *c*, potassium sulphate; *d*, benzophenone, $C_{13}H_{10}O$. Find the percentage deviations

of these values from the measured values, which are, *a*, 0.032; *b*, 0.074; *c*, 0.190; and *d*, 0.31.

Prob. 36.—*Determination of Atomic Weights from Heat-Capacity Measurements.*—Calculate the exact atomic weight of an element whose specific heat-capacity is 0.092, and whose oxide contains 88.82% of the element.

121. Heat-Effects attending Changes in the State of Aggregation of Substances.— The *heat of vaporization* of liquid substances, the *heat of fusion* of solid substances, and the *heat of transition* of one solid substance into another (as of rhombic into monoclinic sulphur) are quantities which are important in themselves and which are frequently involved in calculations of the heat of chemical reactions. The general statement can be made in regard to them that the conversion of the form that is stable at lower temperatures into that stable at higher temperatures (for example, of ice into water, or of rhombic into monoclinic sulphur) is always attended by a positive heat-effect, that is, by an absorption of heat.

The following simple principle, known as *Trouton's rule,* has been discovered in regard to the values of the heat of vaporization: the ratio of the molal heat of vaporization of a liquid at its boiling-point to its boiling-point on the absolute scale has approximately the same value (namely, about 20.5) for all liquids except those whose molecules are associated; that is, $M\bar{L}/T =$ approx. 20.5. The actual values of these quantities in the case of five very different liquids are shown in the following table:

Substance	$M\bar{L}$	T	$M\bar{L}/T$
Bromine	6760	332	20.4
Benzene	7350	353	20.8
Carbon bisulphide	6380	319	20.0
Ethyl ether	6260	308	20.3
Ethyl formate	7180	327	22.0

Substances containing the hydroxyl group, such as water, alcohols, and acids, whose molecules in the liquid state are for other reasons believed to be associated (see Art. 26, Note at end), form marked exceptions to Trouton's rule. Thus the value of $M\bar{L}/T$ is 25.9 for water, 27.0 for ethyl alcohol, and 14.9 for acetic acid.

The molal heat of vaporization of a liquid or solid substance can also be calculated by the approximate form of the Clausius' equation (Art. 22) from the change of its vapor-pressure with the temperature

The *heat of solution* of substances is another important quantity. In determining and expressing it the quantity of solvent in which a definite weight of the substance is dissolved must be taken into consideration. The two limiting cases are the heats of solution in a very large quantity of solvent and in that quantity of solvent which forms with the substance a saturated solution. These two heat-effects sometimes have different signs. They evidently differ by the heat of dilution of the saturated solution with a large quantity of water.

The dissolving of gaseous substances in solvents is always, and that of liquid substances is usually, attended by an evolution of heat; and the dissolving of solid substances in solvents is usually attended by an absorption of heat.

The *heat of dilution* of substances in solution is also important; for it enables the heat of formation of a solution of one concentration to be calculated from that of a solution of another concentration, and thus enables heats of reaction to be calculated at different concentrations. The heat-effect attending the addition of an equal volume of water to a concentrated aqueous solution is often large; but it becomes less as the concentration diminishes; and, after a moderately small concentration (such as 0.2 formal) has been attained, there is usually only a very small heat-effect on adding even a very large quantity of water. For example, on adding at 18° to 1 formula-weight of gaseous HCl or of solid $ZnCl_2$ successively ΔN formula-weights of water, there are evolved the following quantities of heat $(-Q)$ in calories:

ΔN............	5	5	10	30	50	100	200
$-Q$ for HCl...	14960	1200	600	360	120	50	..
$-Q$ for $ZnCl_2$..	7740	1850	1300	2170	1490	820	390

Prob. 37. The heat of fusion of 1 g. of ice at 0° is 79.7 cal. What other data would be needed to calculate the heat-effect attending the melting of 1 g. of ice into 1000 g. of a normal solution of sodium chloride at its freezing-point, —3.42°, and how would the calculation be made?

Prob. 38. The heat of solution at 20° in a large quantity of chloroform of 1 at. wt. rhombic sulphur is +640 cal. and of 1 at. wt. monoclinic sulphur is +560 cal. Show by the law of initial and final states what other heat-effect can be derived from these data, and what its value is.

Prob. 39.—Change of Heat of Reaction with the Concentration.— The heat of solution at 18° of 1Zn in HCl 200Aq is —34,200 cal. Find its heat of solution in HCl 5Aq, *a*, by applying the law of initial and final states, and *b*, by formulating the thermochemical equations involved.

There is another kind of heat of dilution or solution that is of great importance in the thermodynamic treatment of electromotive force and of chemical equilibrium (considered in Chapters VIII and IX). This is the heat-effect attending the addition of one formula-weight of the solvent or solute to an infinite quantity of the solution. The value of this quantity, which is known as the *partial heat of dilution* or *solution,* can be derived from actual data like those given in the preceding table in the ways illustrated by the following problems.

Prob. 40. Determine with the aid of a plot the heat-effect attending the addition of $1H_2O$ to an infinite quantity of $ZnCl_2100H_2O$ at 18°.

Prob. 41. The measured heat-effect Q attending the mixing of $1H_2SO_4$ with NH_2O at 18° is expressed by the empirical equation, $Q = -17860 \, N/(N + 1.80)$ for values of N not exceeding 20. Calculate the heat-effect attending the addition of $1H_2O$ to an infinite quantity of $H_2SO_410H_2O$.

Prob. 42. Derive a relation between the heat-effect attending the dissolving of $1ZnCl_2$ in $100H_2O$, that attending the addition of $100H_2O$ to an infinite quantity of a solution of the composition $1ZnCl_2100H_2O$, and that attending the addition of $1ZnCl_2$ to an infinite quantity of such a solution.

Prob. 43. Calculate the heat-effect attending the addition of:
a, $1ZnCl_2$ to an infinite quantity of $1ZnCl_2100H_2O$.
b, $1H_2SO_4$ to an infinite quantity of $1H_2SO_410H_2O$.

Prob. 44. a. The heat-content of $1ZnCl_2$ is $-97,300$ cal. Calculate the heat-content of $1ZnCl_2$ in $1ZnCl_2100H_2O$ (by which is meant the increase in heat-content in starting with $1Zn$, $1Cl_2$, and an infinite quantity of a solution of the composition $ZnCl_2100H_2O$, and ending with $1ZnCl_2$ in that solution). *b.* Give the values of the other symbols in the thermochemical equations:

$$ZnCl_2100H_2O = ZnCl_2(\text{in } ZnCl_2100H_2O) + 100H_2O(\text{in } ZnCl_2100H_2O) + 0 \text{ cal.}$$
$$ZnCl_2100Aq = ZnCl_2(\text{in } ZnCl_2100H_2O) + 100Aq(\text{in } ZnCl_2100H_2O) + 0 \text{ cal.}$$
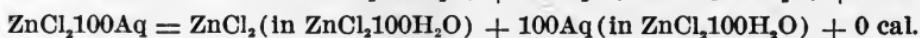
122. Heats of Reaction in Aqueous Solution.

—The investigations made of the heat-effects attending chemical reactions in aqueous solution between substances present at fairly small concentrations (0.1–0.3 normal) have established the following principles:

1. On mixing solutions of two neutral salts which do not form a precipitate by metathesis (for example, solutions of potassium chloride and sodium sulphate) there is scarcely any heat-effect. Exceptions to this principle are met with in the few cases in which an unionized

salt is produced by the metathesis. Thus the metathetical reaction $2K^+Cl^- + Hg^{++}(NO_3^-)_2 = 2K^+NO_3^- + HgCl_2$ is attended by a heat-effect of —12,400 cal.

2. The heat of neutralization of a solution of any largely ionized monobasic acid with a solution of any largely ionized monacidic base (for example, of hydrochloric acid, nitric acid, etc., with sodium hydroxide, potassium hydroxide, etc.) has approximately the same value, whatever be the acid or base. At 18° this nearly constant value averages —13,810 cal. per equivalent when the acid and base solutions are 0.12 to 0.25 normal.

3. When the base or acid is only partly ionized (as in the case of ammonium hydroxide or hydrofluoric acid), the heat-effect attending its neutralization with a largely ionized acid or base is often much larger or smaller than that observed when both acid and base are largely ionized; thus the heat of neutralization of one equivalent of ammonium hydroxide with one of hydrochloric acid is —12,300 cal., and that of one equivalent of hydrofluoric acid with one of sodium hydroxide is —16,300 cal.

4. When one formula-weight of a dibasic acid is neutralized in steps by adding first one equivalent of a largely ionized base and then a second equivalent, the heat-effects for the two equivalents of base are usually different; for example, at 18° the two heat-effects are —14,600 and —16,600 cal. in neutralizing 0.28 normal sulphuric acid with 0.28 normal sodium hydroxide, and they are —11,100 and —9,100 cal. in neutralizing carbonic acid with that base.

5. When certain polybasic acids are neutralized, there is sometimes scarcely any heat-effect when the second or third equivalent of base is added. Thus the successive heat-effects when phosphorous acid (H_3PO_3) is treated with sodium hydroxide at 18° are: —14,800 cal. with the first equivalent, —13,600 cal. with the second equivalent, and only —500 cal. with the third equivalent; and with hypophosphorous acid (H_3PO_2) there is a heat-effect of —15,200 cal. with the first equivalent of sodium hydroxide, and only —110 cal. with the second equivalent.

6. With certain polybasic acids there is a considerable heat-effect when to the solution of the neutral salt another equivalent of base is added; thus, there is a heat-effect of —1200 cal. on mixing a solution

containing one equivalent of sodium hydroxide with one containing one formula-weight of sodium phosphate (Na_3PO_4).

Prob. 45. *a.* Explain the first principle stated in the preceding text with the aid of the ionic theory, assuming that the solutions are very dilute. *b.* What conclusion as to the heat of ionization of neutral salts can be drawn from the fact that this principle holds true even at fairly high concentrations (*e. g.*, 0.3 normal)? *c.* Write a thermochemical equation corresponding to the ionic reaction to which the heat-effect is mainly due in the reaction cited as an exception to the principle.

Prob. 46. Show that on mixing solutions of two salts (such as lead nitrate and potassium iodide) which form a precipitate by metathesis there must be a heat-effect which is substantially equal, but opposite in sign, to the heat of solution of the precipitated substance (the lead iodide).

Prob. 47. *a.* Write the ionic reaction to which the nearly constant heat of neutralization of largely ionized acids and bases corresponds. *b.* What other heat-effect is involved in the neutralization of ammonium hydroxide (a slightly ionized base) with a largely ionized acid, and what is its value? *c.* What is the heat-effect that attends the reaction between $1NH_4Cl$ and $1NaOH$ in 0.2 normal solution?

Prob. 48. Calculate the heat of ionization of one formula-weight of HF from the facts that its heat of neutralization in 0.28 normal solution with 0.28 normal NaOH solution has been found to be —16,300 cal., and its ionization in 0.28 normal solution is estimated to be 5.2%.

Prob. 49. Calculate the heats of ionization at 18° that can be derived from the heats of neutralization of carbonic acid given in the text. Carbonic acid is a very slightly ionized acid; sodium hydrogen carbonate solution is practically neutral; and the sodium carbonate in the 0.07 formal solution produced by the neutralization is 6.3% hydrolyzed.

Prob. 50. Conductance, transference, and reaction-rate measurements have shown that sodium hydrogen sulphate in 0.1 formal solution at 18° consists approximately of 8% $NaHSO_4$, 12% Na_2SO_4, 44% HSO_4^-, 36% $SO_4^=$, and of the corresponding amount of Na^+ and H^+. A calorimetric measurement at 18° has given the result expressed by the equation:

$$NaHSO_4601Aq + NaOH200Aq = Na_2SO_4801Aq + H_2O + 16,620 \text{ cal.}$$

Calculate the heat of the reaction $HSO_4^- = H^+ + SO_4^=$, assuming that the heats of ionization of Na_2SO_4 and of $NaHSO_4$ (into Na^+ and HSO_4^-) are zero.

Prob. 51. What do the heat-effects observed in the neutralization of phosphorous acid and of hypophosphorous acid show as to the existence of salts of these acids in solution?

Prob. 52. Explain the fact stated in the last paragraph of the preceding text.

123. Applications of Thermochemical Principles.

Determination of the Change of the Heat of Reaction with the Temperature.—

Prob. 53. Derive a numerical expression for the heat of ionization of water as a function of the temperature from the following data. The heat evolved on mixing at 18° a solution of 1NaOH in $200H_2O$ with one of 1HCl in $200H_2O$ is 13,810 cal. The specific heat-capacity of the sodium hydroxide solution is 0.9827, that of the hydrochloric acid solution is 0.9814, and that of the sodium chloride solution produced is 0.9887. (It will be noted that the heat-capacity data must be known with great accuracy in the case of reactions between solutes in dilute solution.)

Prob. 54. The heat of formation of 1 mol of gaseous HI at 18° is $+6200$ cal. Estimate the value of its heat of formation at 300° with the aid of the principles relating to the values of heat quantities stated in this chapter, and from the fact that the vapor-pressure of solid iodine is 70 mm. at 109° and 89 mm. at its melting-point, 114°.

Prob. 55.—Heat Evolved by Continuous Processes at High Temperatures.—A mixture of oxygen and hydrogen chloride in the proportion $\frac{1}{4}O_2$: 1HCl at 18° is passed continuously into a vessel at 386° containing a suitable catalyzer. The gas is passed so slowly that equilibrium is established, 80% of the hydrogen chloride being converted into chlorine and water. Calculate the heat that will be actually given off from the equilibrium vessel per mol of HCl passed through.

Maximum Temperature Producible by Chemical Changes.—

Prob. 56. Calculate the maximum temperature that could theoretically be attained in the flame produced by burning at 18° a "water-gas" consisting of equimolal quantities of hydrogen and carbon monoxide with twice the quantity of air required for complete combustion. Assume that there is no loss of heat to the surroundings and that the reaction-products are not appreciably dissociated.

Prob. 57. a. Calculate the maximum temperature and pressure that could be produced by the explosion within a bomb of a mixture consisting of 1 mol H_2, $\frac{1}{2}$ mol O_2, and 1 mol N_2, at 18° and 100 mm., assuming that the water produced is not appreciably dissociated. *b.* The maximum pressure produced in an actual experiment was found to be 840 mm. Show how from this result the degree of dissociation of the water-vapor and the temperature of the mixture at the moment of the explosion can be calculated. (The equations should be formulated, but they need not be solved numerically.)

Prob. 58.—Determination of Chemical Equilibria by Thermochemical Methods.—Describe a thermochemical method of determining the extent to which acetic acid displaces hydrofluoric acid from sodium fluoride in dilute solution. (The heat of neutralization of acetic acid with sodium hydroxide at 18° is —13,230 cal.)

ELECTROCHEMISTRY: THE PRODUCTION OF ELECTRI-
CAL ENERGY BY CHEMICAL CHANGES AND OF
CHEMICAL CHANGES BY ELECTRICAL ENERGY

THE SECOND LAW OF ENERGETICS

124. The Second Law of Energetics.—Before the production of
electrical energy by chemical changes can be adequately considered,
familiarity with certain aspects of another general principle relating
to energy, the so-called second law of energetics, is essential.

The first law of energetics states that when one form of energy is
converted into another the quantity of the form of energy that is pro-
duced is equivalent to the quantity of the form that disappears; but
it does not indicate that there is any other restriction as to the trans-
formability of the different forms of energy. Experience has shown,
however, that while the various forms of work can be completely
transformed into one another and into heat, the transformation of heat
into work is subject to certain limitations. Thus, no system (com-
bination of matter) has ever been discovered which, as a result of any
process taking place continuously in it, can produce work in unlimited
quantity merely by withdrawing heat from the surroundings. An
ideal process which is conceived to produce this result may be called
perpetual motion of the second kind; and the experience just men-
tioned may be expressed by the statement that perpetual motion of
the second kind is impossible. This is the perpetual-motion principle
that was stated and illustrated in Art. 28. Perpetual motion of the
second kind, by which work is conceived to be produced out of heat,
is to be distinguished from perpetual motion of the first kind (described
in Art. 107), by which work is conceived to be produced without con-
suming energy of any kind.

Experience with processes taking place at different temperatures
has led to the conclusion that this principle is a consequence of a
still more general law, known as the *second law of energetics,* which
may be expressed as follows: a process whose final result is only a
transformation of a quantity of heat into work is an impossibility.

Prob. 1. a. State what energy-effects occur when a perfect gas expands at a constant temperature against an external pressure. *b.* Explain why this is not a contradiction of the second law of energetics.

This law does not imply that heat cannot be transformed into work, but only that its transformation must be attended by some other change. This attendant change may consist in a permanent change in the state of the system by which the energy-transformation is brought about; or, when the system undergoes no permanent change in state, it consists in the passage of an additional quantity of heat from a higher to a lower temperature. The latter effect, which can take place only when there is difference of temperature in different parts of the surroundings, will be considered later. In this chapter will be considered only the production of work by changes in state taking place in surroundings of constant temperature.

When the process by which any change in state takes place is one that produces a quantity of work equal to (or differing by only an infinitesimal amount from) the quantity of work which must be expended in order to restore the system to its original state, the process is called a *reversible process.* When the process is one that produces a smaller quantity of work than that which must be expended in restoring the system to its original state, it is called an *irreversible process.* Similarly, when work has to be expended in changing the state of a system, the process is said to be *reversible* when the amount of work expended is equal to that which can be produced when the change in state takes place in the opposite direction, and to be *irreversible* when the amount of work expended is larger than that which can be so produced.

It is to be noted that the term reversible is always employed, in the manner just defined, to designate a process of such a character that it is possible to restore the original condition of things both in the system and its surroundings. After an irreversible process has taken place, it is in general possible to restore the system to its original state, but only by withdrawing from the surroundings a larger quantity of work than was produced in them, so that the original condition in the surroundings is not reproduced. When an irreversible change has once taken place, it is not possible by any means whatever to reproduce in their entirety the conditions that previously existed.

Prob. 2. N mols of a perfect gas having a pressure of 2 atm. are enclosed within a cylinder placed in a thermostat at a temperature T and provided with a weighted piston. The weight on the piston is suddenly reduced, so that it exerts on the gas a pressure of 1 atm., and the gas expands till its own pressure becomes 1 atm. Explain why this process is irreversible; and state what would have to be true of the pressure exerted by the piston on the gas during its expansion in order that the process might be reversible.

Prob. 3. *a.* Derive an expression in terms of N, R, and T for the work produced by the irreversible process described in Prob. 2. *b.* Derive a corresponding expression for the work produced when the same change in state is brought about by a reversible process. *c.* Find the numerical ratio of these two quantities of work.

Prob. 4. Two Daniell cells, each having an electromotive force of 1.10 volts, are connected in series and are used for charging a lead storage-cell having a (counter) electromotive force of 2.10 volts. Explain why the process is not reversible; and state how a number of Daniell cells and a number of storage-cells could be so arranged that the latter might be charged reversibly. (In this case the Daniell cells may be regarded as the system, and the storage cells as a part of the surroundings in which the electrical work is produced and stored.)

As illustrated by the preceding problems, in order that the process by which a change in state is brought about may be reversible, the pressure externally applied must be substantially equal to the pressure exerted by the system itself, or the applied electromotive force must be substantially equal to the electromotive force of the cell. For the change in state will take place in one direction when the applied pressure or electromotive force is only infinitesimally less than that of the system, and in the other direction when it is only infinitesimally greater; but, if the applied pressure or electromotive force were less by a finite amount than that of the system, the quantity of mechanical or electrical work produced in the surroundings would evidently not suffice to restore the system to its initial state; and if the applied pressure or electromotive force were greater than that of the system, more work would be withdrawn from the surroundings than the system would be capable of reproducing on reverting to its original state.

125. Application of the Second Law to Isothermal Changes in State. The Concept of Free Energy.

Prob. 5. In a voltaic cell consisting of one platinum electrode in contact with a 0.1 normal HCl solution and with hydrogen gas at 1 atm. and of a second platinum electrode in contact with the same HCl solution

and with hydrogen gas at 0.1 atm., hydrogen is found to go into solution (as hydrogen-ion) at the first electrode and to be evolved at the second electrode, as a result of the electromotive force which is produced. *a.* Name the change in state that takes place in such a cell when one faraday of electricity passes through it at 18°, specifying all the factors determining the change in state (see Art. 108, first paragraph), but disregarding the transference in the solution, which in a cell of this kind will be shown later to be attended by no energy-effect. *b.* Describe how the same change in state could be brought about reversibly by a process not involving voltaic action. *c.* Show by the perpetual-motion principle that the quantity of work attending this process is equal to the work produced when the same change in state takes place reversibly in the cell.

The principle, illustrated by the preceding problem, that the quantity of work produced or expended when a definite change in the state of a system takes place at a constant temperature by a reversible process is the same whatever be the nature of the reversible process, is of great importance in chemical considerations. This principle shows that any system in any definite state has a certain power of producing work, and that this power changes by a definite amount when a definite change in state takes place. The power of producing work is therefore, like the energy-content and the heat-content, a quantity determined by the state of the system; and, in analogy with the names given to them, it may be called the *work-content* (A) of the system. The absolute value of this quantity cannot be determined; but the change in its value when any definite change in state takes place at a constant temperature is measured by the work (W_R) produced when the change in state takes place reversibly. Thus, representing by A_1 the work-content of the system in the initial state, and by A_2 that in the final state, the decrease in work-content

$$A_1 - A_2 = -\Delta A = W_R.$$

It will be noted that, while the First Law requires that there be a quantity of energy produced in the surroundings equal to the decrease of the energy-content of the system, the Second Law does not require that there be a quantity of work (W) produced equal to the decrease in work-content (as was illustrated by Prob. 3). The Second Law requires only that the quantity of work produced be not greater than the decrease in work-content. That is, $W > -\Delta A$ for no process whatever; $W = -\Delta A$ for a reversible process; and $W < -\Delta A$ for an irreversible one.

Just as it is more convenient in chemical considerations to consider the heat-content rather than the energy-content of systems, so there are many advantages in considering in place of the work-content a quantity which differs from it, just as the heat-content differs from the energy-content, by the value of the pressure-volume product. This quantity, which may be called the *free-energy content* (F), or simply the *free-energy* of the system, is defined by the equation $F = A + p\,v$. Its value is determined by the state of the system, since the values of A and of $p\,v$ are so determined; and the decrease in its value when any change in the state of the system takes place is evidently equal to the work produced when the change takes place reversibly, diminished by the increase of the pressure-volume product; that is,

$$F_1 - F_2 = W_R - (p_2 v_2 - p_1 v_1), \text{ or } -\Delta F = W_R - \Delta(p\,v).$$

The difference $(F_1 - F_2)$ between the free-energy-content of a system in its initial state and that in its final state will be called the free-energy-decrease $(-\Delta F)$ attending the change in state, irrespective of the sign of its numerical value, which may be either positive or negative. The change in state is always considered to take place at some constant temperature.

Prob. 6. a. What is the decrease in joules in the work-content and in the free-energy-content of one formula-weight of water when it changes from liquid water at 100° and 1 atm. to gaseous water at 100° and 1 atm., referring to Prob. 4, Art. 109, for the data needed? *b.* What would be the decrease in these two quantities if the liquid water at 100° and 1 atm. changed to gaseous water at 100° and 1 atm. by a process which produces no work, for example, by introducing the liquid water into an evacuated vessel having a volume equal to that of the saturated vapor?

In cases where different parts of the system are under different pressures, as in the cell of Prob. 5, the decrease in free energy is defined to be the quantity obtained by subtracting from the work produced when the change takes place reversibly the difference between the sum of the $p\,v$ values for all the parts of the system in its final state and the sum of the $p\,v$ values for all its parts in its initial state. Therefore, in general:

$$F_1 - F_2 = W_R - \Sigma(p_2 v_2 - p_1 v_1); \text{ or } -\Delta F = W_R - \Sigma(\Delta p\,v).$$

The principle that the free-energy-decrease attending any process is determined solely by the change in state of the system is the funda-

mental principle on which is based the treatment presented in this book of the subjects of Electrochemistry and Thermodynamic Chemistry. The first step in any application of the principle is therefore to formulate exactly the change in state of the system in terms of its initial and final states; and the next step is to formulate an expression for the free-energy-decrease attending it.

FREE-ENERGY CHANGES ATTENDING CHANGES IN PRESSURE
AND CONCENTRATION

126. Free-Energy Changes attending Changes in Volume and Pressure.—When a system which is under an external pressure equal to its own, so that equilibrium prevails, undergoes an infinitesimal change of volume dv and of pressure dp, the work produced dW_R is equal to $p\,dv$ (Art. 109). The free-energy-decrease $-dF$ attending such a change in state at a constant temperature is, however, by definition equal to $dW_R - d(pv)$. In virtue of the mathematical relation $d(pv) = p\,dv + v\,dp$, the free-energy-decrease attending an infinitesimal change in volume or pressure at a constant temperature is therefore given by the expression:

$$-dF = -v\,dp.$$

Prob. 7. a. Derive an expression for the free-energy-decrease $(-\Delta F)$ attending the change in state of N mols of a perfect gas when at the temperature T its volume and pressure change from v_1 and p_1 to v_2 and p_2. *b.* Formulate an algebraic expression for the decrease of the free energy of N mols of hydrogen when at 18° its pressure changes from 100 atm. to 1 atm. The pressure-volume relations of hydrogen up to high pressures are expressed by the equation $p\,(v - N\,b) = N\,R\,T$, in which b is a constant.

127. Free-Energy Change attending the Transfer of a Substance from a Solution of One Concentration to One of Another Concentration.

Prob. 8. a. Formulate an exact expression (not involving the perfect-gas law) for the free-energy-decrease attending the introduction at the temperature T of m grams of a pure substance at a pressure equal to its vapor-pressure p_0 into an infinite quantity of a solution in which the substance has a vapor-pressure p. Note that this change in state can be brought about by the following reversible process: vaporize the m grams of the substance at the temperature T under a pressure p_0; change the pressure of this vapor to p; and at this pressure condense the vapor into the solution. *b.* Derive from this expression an equation which holds true when the vapor conforms to the perfect-gas law. *c.* Formulate an expression for the free-energy-decrease attending the transfer of N mols of a substance from an infinite quantity of a solution in which its vapor-pressure is p_1 into an infinite quantity of a solution in which its vapor-pressure is p_2.

Prob. 9. Show how the equation formulated in Prob. 8c may be modified so as to contain the mol-fractions x_1 and x_2 of the substance in the two solutions, *a*, when the vapor-pressures p_1 and p_2 conform to Raoult's law: *b*, when these vapor-pressures conform to Henry's law.

c. State in the case of a solution consisting of two substances **A** and **B** the conditions of composition under which Raoult's law and under which Henry's law (and therefore under which the corresponding free-energy expressions) hold true approximately. *d.* Show as in Art. 27 that when the mol-fractions x_1 and x_2 are small, their ratio may be replaced by the ratio of the concentrations c_1 and c_2, which denote the number of mols of the solute per unit-volume of the solvent.

In the preceding problems the following expressions have been derived for the free-energy-decrease which attends the transfer at the temperature T of that quantity of a substance which is N mols in the state of a perfect gas from an infinite quantity of a solution in which its vapor-pressure is p_1, its mol-fraction x_1, and its concentration c_1, into an infinite quantity of another solution in which its vapor-pressure is p_2, its mol-fraction x_2, and its concentration c_2:

$$- \Delta F = N R T \log \frac{p_1}{p_2} \ (1); \quad - \Delta F = N R T \log \frac{x_1}{x_2} \ (2);$$

$$- \Delta F = N R T \log \frac{c_1}{c_2} \ (3).$$

Equation (1) holds true whatever be the mol-fractions or concentrations; but it involves the assumption that the vapor conforms to the perfect-gas law. Equation (2) holds true when, in conformity either with Raoult's law or with Henry's law, the vapor-pressures are proportional to the mol-fractions. Equation (3) holds true when, in conformity with Henry's law, the vapor-pressures are proportional to the mol-fractions and when the latter are small enough to be substantially proportional to the concentrations; it is the expression commonly employed when a solute is transferred from one dilute solution to another.

Since Henry's law applies to the concentrations of a definite molecular species, it is evident that equation (3) must be applied separately to the transfer of each molecular species, not to the transfer of the substance as a whole, if it exists in the solution as two or more different molecular species, as is the case with H^+Cl^- or any other partially ionized substance in aqueous solution, or with acetic acid in benzene solution in which it exists as $C_2H_4O_2$ and $(C_2H_4O_2)_2$. Moreover, although equation (3) was derived by the consideration of a process involving the vaporization of the solute and with the aid of the assumption that the pressure of the vapor was small enough

to conform to the perfect-gas law, yet that equation relates only to the transfer of the substance from one solution to another; and it would be remarkable if its validity depended on whether the substance were volatile or on how large its vapor-pressure might be. In fact, it can be shown, by deriving equation (3) through a consideration of an osmotic process of transferring the substance from one solution to the other, that the equation is exact, provided only that the substance behaves as a perfect solute, as shown by its conformity to the osmotic-pressure equation $P = cRT$ considered in Art. 38.

Prob. 10. *a.* Calculate the free-energy-decrease attending the transfer at 20° of $1NH_3$ from an infinite quantity of a solution of the composition $1NH_3 8\frac{1}{2}H_2O$ in which its vapor-pressure is 80 mm. into an infinite quantity of a solution of the composition $1NH_3 21H_2O$ in which its vapor-pressure is 27 mm. *b.* Calculate the free-energy-decrease attending the dissolving at 20° of $1NH_3$ at 1 atm. in an infinite quantity of a solution of the composition $1NH_3 21H_2O$.

Note.—Throughout this chapter free-energy values are to be expressed in joules. For the gas-constant R its value 8.32 in joules per degree (derived in Prob. 24, Art. 22) must therefore be used.

Prob. 11. Calculate the free-energy-decrease attending the transfer at 20° of $1NH_3$ from an infinite quantity of 0.1 formal NH_4OH solution into an infinite quantity of 0.001 formal NH_4OH solution. The ammonium hydroxide is 1.3% ionized in the 0.1 formal and 12.5% ionized in the 0.001 formal solution, and the remaining ammonium hydroxide is *m* percent dissociated into NH_3 and H_2O in each solution.

Prob. 12. The transfer at the temperature T of one formula-weight of NaCl from an infinite quantity of a dilute solution in which its formal concentration is c_1 and its ionization is γ_1 into an infinite quantity of another dilute solution in which its formal concentration is c_2 and its ionization is γ_2 can be brought about by so transferring either 1 mol Na$^+$ and 1 mol Cl$^-$ or 1 mol unionized NaCl. *a.* Formulate an expression for the free-energy-decrease attending each of these processes. *b.* Show that one of these expressions can be derived from the other with the aid of the mass-action equation for the ionization of the salt. *c.* Calculate the free-energy-decrease by both expressions for the case that the temperature is 18°, the concentrations are 0.0334 and 0.00167 formal, and the ionizations are 0.900 and 0.970.

The large divergence between the values of the free-energy-decrease calculated in Prob. 12 by the two expressions corresponds to the deviations (considered in Art. 86) from the requirements of the mass-action law exhibited by largely ionized substances. It shows that either the

ions or the unionized substance or both deviate considerably from the laws of perfect solutions (thus from the requirements of the osmotic-pressure equation $P = cRT$). It will be seen later (in Prob. 23, Art. 131) that the true value of the free-energy-decrease attending the transfer of the sodium chloride can be directly derived from the electromotive force of a cell containing the two sodium chloride solutions. This true free-energy-decrease is larger by 26 per-cent of its value than that calculated by considering the transfer of the unionized substance; and it is smaller by 3.0 percent of its value than that calculated by considering the transfer of the ions. This result is representative of the behavior of largely ionized uniunivalent substances in general. It shows that the unionized substance deviates very greatly from the laws of perfect solutions, and that a great error would be made if it were assumed to conform to those laws in mass-action or in free-energy calculations. The comparison also shows that the ions deviate considerably from the behavior of perfect solutes; the deviation up to 0.1 formal is, however, not so great as to cause a very serious error in approximate calculations. Therefore, throughout this book, in the case of largely ionized substances, the ions, rather than the unionized substance, are always considered; and the deviation of the activity of the ions of uniunivalent substances from that of perfect solutes up to a concentration of 0.1 formal is disregarded.

In the case of unibivalent salts, such as zinc chloride or sodium sulphate, for which the ionization values are uncertain owing to the probable presence of intermediate ions (referred to Art. 58), the free-energy-decrease attending their transfer from one solution to another can be calculated even approximately only when the concentrations are so small (say less than 0.01 formal) that no great error is made by regarding the ionization as complete.

128. Changes in State in Voltaic Cells.—A change in state can be made to yield electrical energy when it can be brought about by a process of reduction occurring in one place and a process of oxidation occurring in another place; for it is an inherent characteristic of reduction processes that they are attended by a liberation of positive electricity or by an absorption of negative electricity, and of oxidation processes that they are attended by the opposite electrical effects. Thus the reduction of copper-ion to metallic copper may be represented by the equation $Cu^{++} = Cu + 2 \oplus$; and the oxidation of metallic zinc to zinc-ion, by the equation $Zn + 2 \oplus = Zn^{++}$, where the symbol $\oplus$ denotes one faraday of positive electricity. If these two processes occur at the same place, as is the case when metallic zinc is placed in a copper-ion solution, no electrical effect is observed. If, however, the zinc is placed in a zinc-ion solution and the copper in a copper-ion solution, and if the two solutions are placed in contact, the reduction-process tends to occur at one place and to liberate positive electricity there, and the oxidation-process tends to occur at another place and to absorb positive electricity there, thereby producing a difference of potential or an electromotive force between the two places; and if they are now connected by a metallic conductor, a current of electricity will flow through it, and this current can be made to produce work, for example, by passing it through an electric motor. Such an arrangement as that here described, in which an electric current is produced by causing an oxidation-process and a reduction-process to occur at two different places, is known as a *voltaic cell*.

It has been shown in Art. 125 that the quantity of work that can be produced by any process is determined solely by the change in state of the system. Hence the maximum quantity of work producible by the action of a voltaic cell is fully determined by the initial and final states of the substances of which it consists; and in any case under consideration these states, or the corresponding change in state, must be exactly specified. Thus, there must be stated, in addition to the temperature, not merely the chemical reaction that takes place in the cell, but also the conditions of pressure and concentration under which the substances involved in it are produced and destroyed and

any transfers of substances from solutions of one composition to those of another composition.

In order that there may not be a finite change in the concentrations of the solutions, and therefore in the electromotive force of the cell, during the occurrence of the change in state, it will always be assumed that the solutions are present in infinite quantity, so that when a finite quantity of any substance is introduced into or withdrawn from one of the solutions of the cell there is only an infinitesimal change in its concentration.

The character of the cell under consideration will be shown by writing the symbols of the pure substances and solutions in the order in which they are actually in contact with one another, commas being inserted to indicate the junctions at which, as will be explained later, an electromotive force is produced. The conventions described in Art. 113 will be employed to indicate the state of aggregation of substances and the composition of solutions. Thus a cell consisting in series of metallic zinc, of a zinc chloride solution of the composition $ZnCl_2 100H_2O$, of solid mercurous chloride, and of metallic mercury, at a pressure of one atmosphere (as is always understood unless some other pressure is specified), will be represented by the expression:

$$\textbf{Zn, } ZnCl_2 100H_2O, \textbf{ Hg}_2\textbf{Cl}_2 + Hg.$$
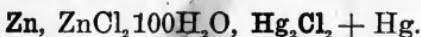
Similarly, a cell whose electrodes are an inert metal **M** in contact with hydrogen gas at 0.1 atmosphere and the same metal in contact with chlorine gas at 0.05 atmosphere, and whose electrolyte is a 0.1 formal HCl solution, will be represented by the expression:

$$\textbf{M} + H_2(\text{1 atm.}), \; HCl(\text{0.1 f.}), \; Cl_2(\text{0.05 atm.}) + \textbf{M}.$$
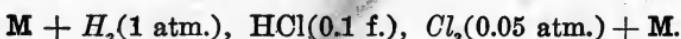
So also a lead storage-cell whose electrodes are lead and an inert metal coated with lead dioxide, and whose electrolyte is a sulphuric acid solution, say of the composition $H_2SO_4 10H_2O$, saturated with lead sulphate, will be represented by the expression:

$$\textbf{Pb} + \textbf{PbSO}_4, \; H_2SO_4 10H_2O, \; \textbf{PbSO}_4 + \textbf{PbO}_2 + \textbf{M}.$$

The change in state taking place in a cell may be expressed by an equation whose left-hand member represents the initial state, and whose right-hand member represents the final state, of the substances involved in the change. Thus the changes of state occurring when at 25° two faradays pass from left to right (as is always understood

unless the opposite is specified) through the first two cells just formulated are shown by the equations:

$$Zn + Hg_2Cl_2 = 2Hg + ZnCl_2(\text{in } ZnCl_2100H_2O) \text{ at } 25°$$
$$H_2(1 \text{ atm.}) + Cl_2(0.05 \text{ atm.}) = 2HCl(\text{at } 0.1 \text{ f.}) \text{ at } 25°.$$
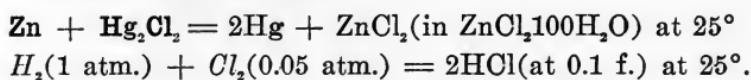
In determining the change in state in the cell it is often well to consider separately the reactions that take place at the two electrodes (see Art. 42) and the ion-transferences that occur in the solutions. The electrode-reactions take place in accordance with Faraday's law (Art. 43), and the transference-effects in accordance with the principles of transference (Arts. 45–49).

Prob. 13. a. State the changes at each electrode and the ion-transferences that attend the passage of two faradays through the first cell formulated above; and show that the net result of these changes is the change in state expressed by the first of the preceding equations. *b.* Do the same for the second cell formulated above.

Prob. 14. a. State the electrode changes and ion-transferences that occur when two faradays pass at 20° through the lead storage-cell formulated above. *b.* Express the resultant change of state that takes place in the cell by an equation.

When, as in these cells, a gaseous or a solid non-metallic substance is in contact with a metal electrode, the adjoining solution is understood to be saturated with that substance. In such cells there are therefore in reality two different solutions, even though for the sake of brevity only one may be written in formulating the cell; thus these cells ought strictly to be written:

$$Zn, \ ZnCl_2100H_2O, \ ZnCl_2100H_2O + Hg_2Cl_2(s.\,f.),^* \ \ Hg_2Cl_2 + Hg.$$
$$M + H_2(1 \text{ atm.}), \ HCl(0.1 \text{ f.}) + H_2(0.00076 \text{ f.}), \ HCl(0.1 \text{ f.}) +$$
$$Cl_2(0.0044 \text{ f.}), \ Cl_2(0.05 \text{ atm.}) + M.$$
$$Pb + PbSO_4, \ H_2SO_410H_2O + PbSO_4(s.f.), \ H_2SO_410H_2O + PbSO_4(s.f.)$$
$$+ \ Pb(SO_4)_2 \ (10^{-8} \text{ f.}), \ \ PbSO_4 + PbO_2 + M.$$
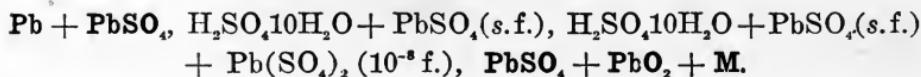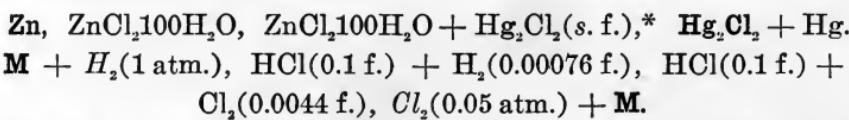
The recognition of the fact that there are in such cells two solutions of slightly different composition is of great importance in considering the mechanism of voltaic action and in evaluating the separate potentials discussed in Arts. 133–137.

When, as in the three cells above considered, the cell contains two solutions of substantially the same composition (in the respects that

*The symbol *s. f.* represents the solubility (in formula-weights per 1000 g. of water) of Hg_2Cl_2 in a solution of composition $ZnCl_2100H_2O$.

in both solutions the ions present at considerable concentrations are the same, that the concentrations of these ions are substantially the same, and that the solvent-medium as a whole is substantially the same), the ion-transferences need not be considered; for, though there is transference from the solution around one electrode to that around the other electrode, there is not an appreciable free-energy change, since the two solutions have substantially the same composition.

Prob. 15. Specify the electrode-changes and ion-transferences and the resultant change in state taking place when one faraday passes through each of the following cells:

　　a. H_2(1 atm.), HCl(0.01 f.), HCl(0.1 f.), H_2(1 atm.).
　　b. Cl_2(1 atm.), HCl(0.01 f.), HCl(0.1 f.), Cl_2(1 atm.).

Note that the transference-effects in these cells are similar to those described in Art. 45, the left-hand solution being regarded as the anode-portion and the right-hand solution as the cathode-portion.

129. Production of Work in Voltaic Cells.—According to a fundamental principle of the science of electricity, when a quantity of positive electricity Q flows between two places, such as the electrodes of a voltaic cell, between which there is a potential-difference or electromotive force E, a quantity of work equal to the product E Q can be produced.

In order that the work produced by a voltaic cell may be the maximum which can be obtained from the change in state taking place in it, the electromotive force at the electrodes must be such that, when it is increased by an infinitesimal amount, the change in state under consideration takes place in the opposite direction. It is this value of the electromotive force which is considered throughout the following pages, and which is called the electromotive force (E) of the cell. In an experimental determination of this electromotive force the assurance must be obtained, by making measurements under various conditions, that the measured electromotive force really corresponds to the change of state under consideration, and not to some incidental process taking place at the electrodes.

Now, according to Faraday's law, the quantity of electricity flowing through a voltaic cell is strictly proportional to the number of equivalents N that are involved in the chemical change at each electrode; that is, Q = N F, where F represents the quantity of electricity (96,500 coulombs) that passes when a reaction involving one equivalent of each of the reacting substances takes place at each electrode.

The electrical work that can be produced by a change in state taking place in a voltaic cell and involving the passage of N faradays of electricity is therefore equal to E N F.

The numerical value of the electromotive force E of the cell will in this book be given a positive sign when the cell tends to produce a current of positive electricity through the cell in the direction in which it is written, and a negative sign when the cell tends to produce such a current in the opposite direction. The symbol N will denote the number of faradays of positive electricity that are considered to pass through the cell from left to right, its numerical value being given a negative sign when positive electricity is considered to pass in the opposite direction. The value of W calculated by the equation will then have, as usual, a positive sign when the cell produces electrical work, and a negative sign when external work is expended upon the cell. The work will be in joules when the electromotive force is in volts and the quantity of electricity in coulombs.

Prob. 16. The electromotive force at 15° of the Daniell cell **Zn, ZnSO$_4$7H$_2$O + ZnSO$_4$$n'H_2$O, CuSO$_4$$n''H_2$O + CuSO$_4$5H$_2$O, Cu** is 1.093 volts. What must be the values of NF in coulombs and of W in joules in order to precipitate 1 at. wt. of zinc; and what does the sign of each of these quantities signify?

When a voltaic cell acts reversibly there is ordinarily produced, in addition to the electrical work, a quantity of mechanical work corresponding to the changes in volume of the different parts of the cell taking place under their respective pressures. The total work W_R is therefore E N F $+ \Sigma(p\Delta v)$. Since by Art. 125 the free-energy-decrease is equal to $W_R - \Sigma(\Delta p\, v)$, it is equal simply to the electrical work that can be produced. That is, for any change in state taking place in a voltaic cell under constant pressures:

$$-\Delta F = \text{E N F}.$$

Prob. 17. Calculate exact values of the electrical work and the mechanical work that are produced when 1 faraday passes under reversible conditions through the cell H_2(1 atm.), HCl(0.1 f., 1 atm.), Cl_2 (0.05 atm.) at 25°. The electromotive force of this cell is 1.451 volts. The increase in the volume of an infinite quantity of 0.1 f. HCl solution caused by introducing 1HCl into it is 18.7 ccm. What is the corresponding free-energy-decrease?

130. Change of the Electromotive Force of Voltaic Cells with the Concentration of the Solutions.—The considerations of the preceding articles make it possible to calculate the change that is produced in the electromotive force of a cell by varying the concentration of the solutions contained in it. Thus the difference between the electromotive force of the cell H_2(1 atm.), HCl(0.01 f.), Cl_2(1 atm.) and that of the cell H_2(1 atm.), HCl(0.1 f.), Cl_2(1 atm.) can be derived by considering that one faraday passes through these two cells arranged in series in opposition to each other, by noting what the resultant change in state is, and by equating the two expressions for the attendant free-energy-decrease derived in preceding articles.

Prob. 18. Calculate the difference between the electromotive forces at 18° of the two cells named in the preceding text. The ionizations of the acid in the two solutions are 0.972 and 0.925.

Prob. 19. Calculate the difference between the electromotive forces at 25° of the cells H_2(1 atm.), HCl9H_2O, Cl_2(1 atm.) and H_2(1 atm.), HCl16.7H_2O, Cl_2(1 atm.). The vapor-pressures of HCl in the two solutions at 25° are 0.0550 and 0.0044 mm.

Prob. 20. State what data are needed in order to calculate the electromotive force E_1 at 18° of the cell H_2(1 atm.), H_2SO_4(10 f.), O_2(1 atm.) from that E_2 of the cell H_2(1 atm.), H_2SO_4(0.01 f.), O_2(1 atm.); and formulate an expression by which the calculation could be made.

Prob. 21. The cell **Ag + AgCl**, HCl(0.1 f.), Cl_2(1 atm.) has at 25° an electromotive force of 1.142 volts. How much would its electromotive force be changed by substituting HCl(0.01 f.) for the HCl(0.1 f.)?

131. The Electromotive Force of Concentration-Cells.—A cell which consists of two identical electrodes and of two solutions containing the same substance at two different concentrations is cal'ed a *concentration-cell*. The cell **Zn**, $ZnCl_2$(0.01 f.), $ZnCl_2$(0.001 f.), **Zn** is an example of a concentration-cell; so also are the cells formulated in Prob. 15.

Prob. 22. a. Derive an algebraic expression for the electromotive force of the cell H_2(1 atm.), HCl(c' f.), HCl(c'' f.), H_2(1 atm.), where the concentrations c' and c'' are small, by considering (as in Prob. 15) the change in state that occurs in the cell when N faradays pass through it and by considering the two expressions for the attendant free-energy-decrease derived in preceding articles. *b.* Calculate the electromotive force of the cell at 18° when the concentrations c' and c'' are 0.01 and 0.1 formal. For the ion-conductances see Art. 56.

Prob. 23. *a, b.* Answer the same questions as in Prob. 22 for the cell Cl_2(1 atm.), HCl(c' f.), HCl(c'' f.), Cl_2(1 atm.).

Prob. 24. Formulate a numerical expression by which the electromotive force of the cell Zn, $ZnCl_2$(0.01 f.), $ZnCl_2$(0.001 f.), Zn at 18° can be calculated. Consider the ionization of the salt in both solutions to be complete. (See the last paragraph of Art. 127.)

Prob. 25. Calculate the electromotive force at 18° of the cell Ag + AgCl, NaCl(0.0334 f.), NaCl(0.00167 f.), AgCl + Ag, using the data of Prob. 12c. (The electromotive force of this cell has been experimentally determined and found to be 0.05614 volt.)

Another type of concentration-cell is that in which there is a single aqueous solution in contact with electrodes consisting of some metal dissolved at two different concentrations in mercury. For example, the cell Zn 100Hg, $ZnCl_2$ 100H_2O, Zn 200Hg is of this type. Since most of the metals dissolved at small concentrations in mercury have been shown by vapor-pressure and freezing-point measurements to be nearly perfect solutes having monatomic molecules, the electromotive force of cells having such solutions as electrodes can be calculated with the aid of the preceding considerations.

Another similar type of concentration-cell is that in which the two electrodes consist of some inert metal surrounded by the same gas at two different pressures, as is the case in the hydrogen cell of Prob. 5 and in the oxygen cell M + O_2(1 atm.), KOH(1 f.), O_2(0.1 atm.) + M.

Prob. 26. Calculate the electromotive force at 18° of the zinc-mercury cell formulated in the preceding text.

Prob. 27. Calculate the electromotive force at 25° of the oxygen cell formulated in the preceding text.

ELECTROMOTIVE FORCE OF CELLS INVOLVING CHEMICAL CHANGES.
ELECTRODE–POTENTIALS AND LIQUID–POTENTIALS

132. Chemical Changes in Voltaic Cells.—In the cells thus far considered the change of state consists only in a transfer of one or more of the substances from one pressure or concentration to another. In most voltaic cells, however, a chemical change takes place. Thus in the Daniell cell the reaction $Zn + CuSO_4 = Cu + ZnSO_4$ occurs. Other examples of cells in which similar chemical changes take place are given in Art. 128.

A chemical change somewhat different in character from those just considered takes place in cells whose half-cells consist, not of solid or gaseous elementary substances in contact with solutions of their ions, but of an inert metal electrode in contact with two solutes in different stages of oxidation. Thus the electrode-reactions in the cell **M**, $Fe^{++}Cl^-_2(c_1) + Fe^{+++}Cl^-_3(c_2)$, $Cl^-(c_3) + Cl_2(c_4)$, **M**, attending the passage of one faraday are $Fe^{++} + \oplus = Fe^{+++}$ and $\frac{1}{2}Cl_2 = Cl^- + \oplus$, and the whole reaction is $Fe^{++}Cl^-_2 + \frac{1}{2}Cl_2 = Fe^{+++}Cl^-_3$. Such cells do not, however, require special treatment; for the principles applicable to other cells can be readily extended to them, as will be seen in the following articles.

Evidently, if the free-energy-decrease attending the chemical change in any cell could be determined by any independent method, the electromotive force of the cell could be found with the aid of the equation $-\Delta F = E N F$. There is, in fact, such a method by which the free-energy-decrease attending a chemical change can be calculated when the pressures or concentrations involved are small. This method will be considered in the following chapter.

In this chapter will be presented only the electromotive-force side of the problem. There remains therefore to be considered only the partial electromotive forces at the different junctions within the cell. The consideration of these is important in two respects: first, it shows more clearly the separate factors which determine electromotive force: and secondly, it enables the electromotive force of a great number of cells to be calculated from a relatively small number of experimentally determined constants.

133. The Electrode-Potentials of Voltaic Cells.—The electromotive force produced by a voltaic cell is the sum of the electromotive forces

produced at the junctions between the electrodes and the solutions and of those produced at the junctions between the different solutions that may be present in the cell. Thus the electromotive force of the Daniell cell is the algebraic sum of the electromotive force from the zinc to the zinc-sulphate solution, that from the zinc-sulphate solution to the copper-sulphate solution, and that from the copper-sulphate solution to the copper. The electromotive forces at the electrodes are commonly called *electrode-potentials;* and those at the junctions of the solutions, *liquid-potentials.*

Although attempts have been made to determine by certain experimental methods the absolute values of electrode-potentials, yet the measurements made by these methods are not nearly so accurate nor reliable as those of the electromotive force of ordinary cells. It is therefore customary to adopt as the value of the electrode-potential of any half-cell (such as Zn, $ZnCl_2 100H_2O$) the electromotive force of the whole cell which consists of the half-cell under consideration combined with a standard half-cell. The electrode-potential of the standard half-cell is thereby arbitrarily assumed to be zero. Three different half-cells are in use as such standards of reference; namely, the half-cell Hg, $Hg_2Cl_2 + KCl$(1 n.), the half-cell H_2(1 atm.), H_2SO_4 (2 n.), and the half-cell H_2(1 atm.), H^+(1 m.). The first of these cells, which is commonly called the *calomel-electrode,* has certain experimental advantages. The last of these cells, which will be here called the *molal hydrogen-electrode,* has the simplest theoretical significance. The exact difference between the electrode-potentials of these standard half-cells will be shown later.

The electrode-potential of any half-cell is therefore equal to the electromotive force of the whole cell formed by combining it with one of these standard half-cells. Thus the electrode-potential of the half-cell Zn, $ZnCl_2 100H_2O$ referred to the calomel-electrode is equal to the electromotive force of the whole cell Zn, $ZnCl_2 100H_2O \mid\mid KCl$(1 n.) $+ Hg_2Cl_2$, Hg. Similarly the electrode-potential of the half-cell Cl_2 (1 atm.), HCl(0.1 f.) referred to the molal hydrogen-electrode is equal to the electromotive force of the cell Cl_2(1 atm.), HCl(0.1 f.) $\mid$ H^+(1 m.), H_2(1 atm.). It is, however, further understood that in evaluating this electromotive force the liquid-potential has been subtracted from the measured electromotive force of the whole cell—a

fact which is indicated in the symbolic representation of the cell by inserting parallel lines, instead of a comma, at the liquid junction.

It will be noted that the electrode-potential has a positive sign when positive electricity tends to flow from the electrode to the solution, and a negative sign when it tends to flow in the opposite direction. In the case of liquid-potentials the same convention as to sign is adopted as in the case of whole cells; namely, the liquid-potential is given a positive sign when positive electricity tends to flow from the solution whose symbol is written on the left-hand side to the solution whose symbol is written on the right-hand side; and it is given a negative sign in the reverse case. (In using data from outside sources, it is to be noted that foreign electrochemists employ the opposite convention as to the sign of electrode-potentials.)

Prob. 28. Measurements of the electromotive forces at 25° of the cells

H_2(1 atm.), HCl(0.1 n.), KCl(0.1 n.), KCl(1 n.), **Hg_2Cl_2 + Hg,**

Cl_2(1 atm.), HCl(0.1 n.), KCl(0.1 n.), KCl(1 n.), **Hg_2Cl_2 + Hg,**
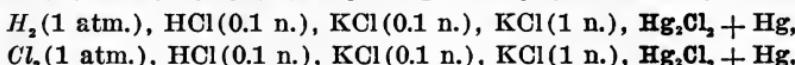
have given the values 0.3740 and —1.114 volts, respectively. The liquid-potential of KCl(0.1 n.), HCl(0.1 n.) has been found to be —0.0283 volt; and that of KCl(0.1 n.), KCl(1 n.) is probably about 0.001 volt. *a.* Find the values of the electrode-potentials that can be derived from these data. *b.* Calculate the electromotive force of the cell H_2(1 atm.), HCl(0.1 n.), Cl_2(1 atm.).

134. Change of Electrode-Potentials with the Ion-Concentrations. Concept of Specific Electrode-Potentials.—Just as the total electromotive force of a cell is determined solely by the change in state that takes place in it, so any electrode-potential is determined solely by the change in state that takes place at the electrode. With the aid of this principle and the general expressions for free-energy-decrease derived in Arts. 127 and 129, the change of an electrode-potential with the concentration of the ions or with that of any other gaseous or dissolved substance involved in the electrode-reaction can readily be calculated, provided the concentrations are so small that the dissolved substances conform to the laws of perfect solutes.

Prob. 29. Derive an algebraic expression for the difference $E_x - \bar{E}_x$ between the electrode-potentials of the two half-cells involved in each of the following cells, by considering the change in state that occurs when one faraday is passed through the cell and assuming that the dissolved substances behave as perfect solutes up to a concentration of 1-molal:

a. O_2(p atm.), OH⁻(c m.), OH⁻(1 m.), O_2(1 atm.).

the two electrode-potentials involved in each of the following cells:

c. Hg + Hg_2SO_4, $SO_4^=$(c m.), $SO_4^=$(1 m.), Hg_2SO_4 + Hg.

b. **Ag** + **AgCl**, Cl⁻(c m.), Cl⁻(1 m.), **AgCl** + **Ag**.

e. Cl_2(p atm.), Cl⁻(c m.), Cl⁻(1 m.), Cl_2(1 atm.).

    Prob. 30. Derive an algebraic expression for the difference between

a. **Ag**, Ag⁺(c m.), Ag⁺(1 m.), **Ag**.   *b.* **Zn**, Zn⁺⁺(c m.), Zn⁺⁺(1 m.), **Zn**.

c. Hg, Hg_2^{++}(c m.), Hg_2^{++}(1 m.), Hg.   *d.* **I₂**, I⁻(c m.), I⁻(1 m.), **I₂**.

d. **M**, Cl_2(c_1 m.) + Cl⁻(c_2 m.), Cl_2(1 m.) + Cl⁻(1 m.), **M**.

e. **M**, Fe⁺⁺(c_1 m.) + Fe⁺⁺⁺(c_2 m.), Fe⁺⁺(1 m.) + Fe⁺⁺⁺(1 m.), **M**.

The electrode-potential calculated as in the preceding problems for the case that the concentrations of the ions or other solutes involved in the electrode-reaction are 1 molal and the pressure is one atmosphere is called the *specific electrode-potential*. It will be here represented by the symbol Ē followed by a subscript showing the element involved in the electrode-reaction, or, when necessary for clearness, by a parenthesis showing both substances involved in that reaction; for example, by such symbols as $\bar{E}_{Zn}$, $\bar{E}_{H}$, $\bar{E}(Cl_2, Cl^-)$, $\bar{E}(Fe^{++}, Fe^{+++})$, $\bar{E}(Ag + AgCl, Cl^-)$. Its value is not that actually observed when the concentrations are 1 molal, owing to the large deviation (discussed in Art. 86) of the activity of ions from that of perfect solutes at such high concentrations. It is to be regarded as an empirical constant derived from measurements at small concentrations, from which conversely the true electrode-potential at any small concentration can be calculated.

It is evident from the preceding problems that in general the electrode-potential $E(A, B, ..)$ when the concentrations of the solutes $A, B, ..$ involved in the electrode-reaction are $c_A, c_B, ...$ is related to the specific electrode-potential $\bar{E}(A, B, ..)$ in the way expressed by the equation:

$$E(A, B, ..) = \bar{E}(A, B, ..) - N_A \frac{RT}{F} \log c_A - N_B \frac{RT}{F} \log c_B - ..$$

where $N_A, N_B, ...$ represent the number of mols of the solutes **A, B,..** which are produced when one faraday of positive electricity passes from the electrode to the solution, the value being given a negative sign for any solute which is destroyed instead of being produced. When one of the substances involved in the electrode-reaction is a gas its concentration may be replaced by its pressure, the specific electrode-

potential in that case being the electrode-potential when the gas is at a pressure of one atmosphere. For convenience in numerical calculations it may be noted that the constant $2.303\,R/\text{F}$ (equal to $2.303 \times 8.32/96500$) has the value 1.984×10^{-4}.

Prob. 31.—Determination of Specific Electrode-Potentials.—Calculate the specific electrode-potentials at 25°, referred to the calomel-electrode, of a, H_2, H^+; b, $Cl_2\,Cl^-$; c, **Ag + AgCl**, Cl^-; d, **Ag, Ag⁺.** For the electromotive-force values needed see Probs. 28 and 21. The ionization of HCl at 0.1 normal is 92%. The solubility of silver chloride in water at 25° is 1.30×10^{-5} normal.

The specific electrode-potential of H_2, H^+ referred to the calomel-electrode has been calculated in the preceding problem. From data for similar cells with more dilute HCl solutions its value has been more accurately determined, and found to be $+0.277$ volt at 25°. This potential is evidently the electrode-potential of the molal hydrogen-electrode, $H_2(1\text{ atm.})$, $H^+(1\text{ m.})$, mentioned in Art. 133 as one of the standard half-cells. It is, to be sure, not the actual potential of this half-cell; but it is the potential that is calculated for it by the usual logarithmic formula from the electrode-potential of any half-cell $H_2(1\text{ atm.})$, $H^+(c\text{ m.})$ in which the concentration c is very small.

This molal hydrogen-electrode will be used as the standard of reference throughout this book, because of its simple theoretical significance. Its potential at 25° is substantially identical, so far as can be judged from existing data, with that of the half-cell $H_2(1\text{ atm.})$, $H_2SO_4(2\text{ n.})$, which is often employed as the standard hydrogen-electrode. The value of any electrode-potential at 25° referred to this standard is evidently 0.277 volt smaller than the value of the same electrode-potential referred to the calomel-electrode.

135. Values of the Specific Electrode-Potentials.—The following table contains some of the more accurately determined values of the specific electrode-potentials at 25° and one atmosphere, referred to that of the molal hydrogen-electrode taken as zero.

Li, Li⁺	3.027	Cu⁺, Cu⁺⁺	—0.20	Fe⁺⁺, Fe⁺⁺⁺	—0.740
K, K⁺	2.931	Ag, AgCl + Cl⁻	—0.224	Ag, Ag⁺	—0.793
Na, Na⁺	2.721	Hg, Hg₂Cl₂ + Cl⁻	—0.270	Hg, Hg₂⁺⁺	—0.80
Zn, Zn⁺⁺	0.76	Cu, Cu⁺⁺	—0.34	Hg₂⁺⁺, Hg⁺⁺	—0.92
Fe, Fe⁺⁺	0.43	O₂, OH⁻	—0.393	Br₂(1 m.), Br⁻	—1.10
Cd, Cd⁺⁺	0.40	Cu, Cu⁺	—0.51	Cl₂, Cl⁻	—1.357
Pb, Pb⁺⁺	0.13	I₂, I⁻	—0.533	Cl₂, Cl⁻	—1.388

Specific electrode-potentials which are related to one another can be calculated in the ways illustrated by the following problems.

Prob. 32. State what data would be needed to calculate one of the following specific electrode-potentials from the other, and formulate an expression by which the calculation could be made: *a*, Cl_2, Cl^- from Cl_2, Cl^-; *b*, Hg, Hg_2Cl_2 + Cl^- from Hg, Hg_2^{++}.

Relation between the Specific Electrode-Potentials of an Element that exists in More than Two States of Oxidation.—

Prob. 33. By considering the effect of passing electricity through the cells **Cu**, $Cu^+(1 m.)$ || $Cu^{++}(1 m.)$, **Cu**, and **Cu**, $Cu^{++}(1 m.)$ || $Cu^+(1 m.)$ + $Cu^{++}(1 m.)$, **M**, derive a relation between the specific electrode-potentials of **Cu**, Cu^+; Cu^+, Cu^{++}; and **Cu**, Cu^{++}; and calculate the last of these potentials from the first two.

Prob. 33A. a. By considering appropriate cells derive an expression for the specific electrode-potential of Hg, Hg^{++} in terms of those of Hg, Hg_2^{++} and of Hg_2^{++}, Hg^{++}. *b.* Calculate the value of the first of these potentials from the values of the other two which are given in the preceding table.

136. Calculation of the Electromotive Force of Cells from the Specific Electrode-Potentials.—The electromotive force of cells in which the liquid-potentials are negligible or are to be disregarded can be calculated from the specific electrode-potentials in the way illustrated by the following problems.

Prob. 34. Calculate the electromotive force at 25° of the cell **Zn**, $ZnCl_2(0.001 f.)$, **AgCl + Ag**. Consider the ionization of the zinc chloride to be complete.

Prob. 35. Calculate the electromotive force at 25° of the cell $H_2(0.1 atm.)$, $H_2SO_4(0.05 f.)$, **$PbSO_4$ + Pb**. The saturated solution of $PbSO_4$ at 25° is 0.00014 formal. In regard to the ionization of sulphuric acid see Prob. 38, Art. 60.

Prob. 36. Formulate numerical expressions for calculating the electromotive force at 25° of each of the following cells:

a. **M + CuCl**, $CuCl_2(0.01 f.)$, $Cl_2(0.1 atm.)$.

b. **M**, 0.01 f. KI sat. with I_2 || $FeCl_2(0.02 f.)$ + $FeCl_3(0.01 f.)$, **M**. Regard the ionization of all the salts as complete. The solubility of CuCl is 0.0010 formal. For the composition of iodide solutions saturated with iodine see Prob. 52, Art. 92.

137. Evaluation of Liquid-Potentials.—Just as the electromotive force of a whole cell is determined by the free-energy-decrease attending the change in state that takes place in the cell, and just as the electrode-potential is determined by the free-energy-decrease attend-

ing the change in state that takes place at the electrode, so a liquid-potential is determined by the free-energy-decrease attending the change in state that takes place at the boundary between the two solutions.

The change in state at such a boundary is of a simple character in the case where the two solutions contain only the same solute at two different concentrations, as in the combination, NaCl(0.01 f.), NaCl(0.1 f.). In this case the calculation is based on the consideration of the number of equivalents of the positive ion-constituent and of the negative ion-constituent that pass through the boundary in the two opposite directions per faraday passed through. It therefore involves a knowledge of the transference-numbers of the ions. It also involves, since the free-energy-decrease attending the transference of the ions must be evaluated, a knowledge of the ion-concentrations in the two solutions.

Prob. 37. Calculate the liquid-potential at 18° of the combinations: *a*, NaCl(0.1 f.), NaCl(0.01 f.) ; *b*, K₂SO₄(0.1 f.), K₂SO₄(0.01 f.). For the data needed see Arts. 53 and 56.

*By a similar consideration of the ion-transference that takes place at the boundary of the two solutions an expression can be derived for the liquid-potential of combinations of the types KCl, KOH; KCl, NaCl; K₂SO₄, Na₂SO₄; ZnSO₄, CuSO₄; for the case that the two solutes have the same concentration and ionization. Namely, taking as a specific example the combination KCl(*c* formal), NaCl(*c* formal), it will be noted that there must be at the boundary a portion of the solution in which the two salts are present in varying proportions, the concentration of the potassium chloride decreasing continuously from left to right from *c* to 0, and that of the sodium chloride increasing continuously in the same direction from 0 to *c*. Representing now by T_K and T_{Na} the transference-numbers of the respective ions in the two solutions of the pure salts, it is evident that per faraday of electricity T_K equivalents of potassium-ion enter the left-hand side of the boundary-portion, and that no potassium-ion leaves the right-hand side of that portion; that no sodium-ion enters the left-hand side, but that T_{Na} equivalents of sodium-ion leave the right-hand side; and that $1—T_K$ equivalents of chloride-ion leave the left-hand side and $1—T_{Na}$

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*This paragraph and the problem following it may be omitted in brief courses.

equivalents of chloride-ion enter the right-hand side of the boundary-portion. The resultant change in state attending the passage of one faraday is therefore the transfer of T_K equivalents of KCl from the pure potassium chloride solution (where its concentration is c) into the boundary-portion (where its concentration has values varying from c to 0), and the transfer of T_{Na} equivalents of NaCl from the boundary-portion (where its concentration has values varying from 0 to c) into the pure sodium chloride solution (where its concentration is c). The free-energy-decrease attending these transfers is in this case an integral of an infinite number of infinitesimal free-energy-changes. By evaluating it and placing it equal to the electrical work that attends these transfers when they are brought about by the passage of the current, an expression for the liquid-potential is obtained.

Prob. 38. Describe in detail the change in state that takes place when one faraday passes through the combination $Cu(NO_3)_2(0.01\text{ f.})$, $Zn(NO_3)_2(0.01\text{ f.})$.

The general expression, obtained in the way just described, for the liquid-potential E_L between solutions of any two substances of the same ionic type having one ion in common and having equal concentrations and ionizations is:

$$E_L = \frac{R\,T}{\nu\,F} \log \frac{\Lambda_{01}}{\Lambda_{02}}.$$

In this expression Λ_{01} and Λ_{02} denote the equivalent conductances at zero concentration of the left-hand and right-hand solutes, respectively, and ν denotes the number of positive charges on the ions not common to the two solutes, it being given a negative value when the charges are negative. In the derivation of this equation it is assumed that intermediate or complex ions are not present, and that the simple ions behave as perfect solutes and have the same relative conductances up to the concentration involved.

Prob. 39. Calculate the liquid-potential at 18° of: a, $KOH(0.1\text{ f.})$, $KCl(0.1\text{ f.})$; b, $HCl(0.01\text{ f.})$, $KCl(0.01\text{ f.})$; c, $ZnSO_4(0.1\text{ f.})$, $CuSO_4(0.1\text{ f.})$.

Prob. 40. Calculate the electromotive force at 18° of the cell Ag, $AgNO_3(0.1\text{ n.})$, $KNO_3(0.1\text{ n.})$, $KCl(0.1\text{ n.})$, $KCl(1\text{ n.}) + Hg_2Cl_2$, Hg. Assume that the potassium chloride is 74% ionized at 1 normal and 84% ionized at 0.1 normal, and that the other two salts are 84% ionized at 0.1 normal.

For combinations of solutions of two salts having a common ion but different concentrations, such as KNO_3(0.1 n.), KCl(0.01 n.), and for combinations of solutions of salts without a common-ion, such as KNO_3(0.1 n.), $NaCl$(0.01 n.), the calculation of the liquid-potential is very complicated. Combinations of these kinds can, however, be avoided, as illustrated by the cell of Prob. 40, by connecting the two solutions through intermediate ones so as to produce only combinations of the two types for which the liquid-potentials can be calculated as described above.

It is to be noted that the above-derived expressions for the liquid-potentials involve the assumption that the ions behave as perfect solutes, and therefore that these expressions are exact only at small concentrations. The assumption is also involved in the case of tri-ionic salts that these are ionized only into the ultimate ions (such as K^+ and $SO_4^=$), without formation of an appreciable proportion of the intermediate ion (such as KSO_4^-).

A liquid-potential can sometimes be experimentally determined by measuring the electromotive force of a cell involving it in which the two electrode-potentials are made substantially equal, as in the cells:

$Hg + Hg_2Cl_2$, KCl(0.1 f.), $NaCl$(0.1 f.), $Hg_2Cl_2 + Hg$.

Ag, $AgNO_3$(0.001 f.) $+ KNO_3$(0.1 f.), $AgNO_3$(0.001 f.) $+$
$NaNO_3$(0.1 f.), Ag.
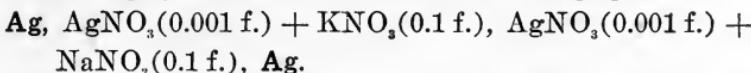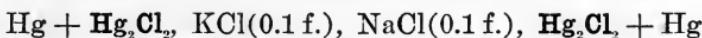
Prob. 41. a. Show that the electromotive force of the silver cell here formulated is substantially equal to the liquid-potential of KNO_3(0.1 f.), $NaNO_3$(0.1 f.), by specifying exactly what determines each of the three partial potentials of the cell. *b.* Show why there would be a considerable error in deriving the liquid-potential of KNO_3(0.1 f.), $NaNO_3$(0.01 f.) from the electromotive force of a cell which differs from the one just considered only in the respect that the $NaNO_3$(0.1 f.) is replaced by $NaNO_3$(0.01 f.).

138. Determination of Ion-Concentrations and of Equilibrium-Constants Involving Them by Means of Electromotive-Force Measurements.

*Prob. 42.—Determination of Solubility.—*The electromotive force of the cell $Ag + AgI$, KI(0.1 f.), KNO_3(0.1 f.), $AgNO_3$(0.1 f.), Ag is 0.814 volt at 25°. Calculate the solubility of silver iodide in water at 25°. Assume the ionizations of all the substances to be equal and to have the average value shown by salts of the uniunivalent type (given in Art. 58).

Prob. 43.—Determination of the Ionization-Constant of Water.— Calculate the ionization-constant of water (Art. 85) at 18° from the fact that the electromotive force of the cell H_2(1 atm.), HCl(0.1 f.), KCl(0.1 f.), KOH(0.1 f.), H_2(1 atm.) is —0.653 volt at 18°. Make the same assumption in regard to the ionizations as in the preceding problem.

Prob. 44.—Determination of Complex-Constants.— The electromotive force of the cell **Ag**, $K^+Ag(CN)_2^-$ (0.01 n.) + KCN(1 n.), KCl(1 n.), Hg_2Cl_2 + Hg is 0.83 volt at 25°. Calculate the dissociation-constant of the complex-ion $Ag(CN)_2^-$ at 25°. Assume the ionization of the salts to be 74%, and neglect the liquid-potential, which is small in this case.

Prob. 45.—Determination of the Hydrolysis of Salts.— When a solution 0.05 formal in Na_2HPO_4 is saturated with hydrogen at 1 atm., when a platinum electrode is placed in it, and when the half-cell HCl(0.01 f.) + NaCl(0.1 f.), H_2(1 atm.), is brought into contact with it, the cell thus formed is found to have at 18° an electromotive force of 0.398 volt. Calculate the hydrolysis of the salt, assuming complete ionization of the largely ionized substances, and neglecting the liquid-potential, which is made small by the addition of the sodium chloride.

Prob. 46.—Determination of Indicator-Constants.— When the Na_2HPO_4 solution of Prob. 45 is made 0.0001 formal in phenolphthalein the indicator is found to show a color 13% as intense as that which is produced on adding to the solution an excess of sodium hydroxide. Calculate the ionization-constant of this indicator.

139. Derivation of the Equilibrium-Conditions of Oxidation Reactions from the Electrode-Potentials.—When the concentrations of the substances involved in the two electrode-reactions are such that the two electrode-potentials are equal to each other, there is evidently no tendency for the cell to act nor for the chemical change to take place in it. In other words, the concentrations that make the two electrode-potentials equal are concentrations at which the chemical change is in equilibrium. The equilibrium-constant of the chemical change which is the resultant of the two electrode-reactions can therefore be calculated from the specific electrode-potentials.

Prob. 47. Calculate the concentration of copper-ion at which the reaction $Zn + Cu^{++} = Cu + Zn^{++}$ is in equilibrium when the zinc-ion is 1 molal.

Prob. 48. a. Calculate the concentration of hydrogen-ion at which the reaction $Pb + 2H^+Cl^- = H_2 + Pb^{++}Cl_2^-$ is in equilibrium at 25° when the hydrogen has a pressure of 1 atm. and the lead-ion is 0.03 molal. *b.* Formulate an algebraic relation between the equilibrium-constant of the corresponding ionic reaction and the specific electrode-potentials. *c.* Calculate the value of this equilibrium-constant.

Prob. 49. *a.* Formulate an algebraic relation between the equilibrium-constant of the ionic reaction $Ag + Fe^{+++} = Ag^+ + Fe^{++}$ and the specific electrode-potentials involved. *b.* Calculate the value of this equilibrium-constant. *c.* Calculate the composition of the equilibrium-mixture that results when metallic silver is placed in 0.1 formal $Fe(NO_3)_3$ solution, assuming complete ionization of the salts.

Prob. 50. Formulate a complete numerical expression for calculating the OH^- concentration at which 1000 times as much manganate-ion ($MnO_4^=$) as permanganate-ion (MnO_4^-) is present in contact with air when equilibrium is reached at 25°. The specific electrode-potential of $MnO_4^=$, MnO_4^- has been roughly determined to be —0.61 volt at 25°.

Prob. 51. *a.* Derive an expression for the equilibrium-constant of the reaction $Cu + Cu^{++} = 2 Cu^+$ in terms of the specific electrode-potentials. *b.* Calculate the concentration of cuprous salt resulting when copper is shaken with a 0.1 formal $CuSO_4$ solution at 25°, assuming complete ionization. *c.* Calculate the concentration of cupric salt in the equilibrium-mixture produced by shaking a 0.1 formal $CuCl_2$ solution with copper at 25°.

140. Electromotive Force of Cells with Concentrated Solutions.—

The electromotive force of any cell in which solutes are present at large concentrations cannot be calculated from the specific electrode-potentials with the aid of the logarithmic concentration formula of Art. 134, since this holds true even approximately only when the concentration does not exceed about 0.1 normal. A knowledge of the change in state taking place in such a cell and of the reactions occurring at its electrodes is, however, of importance, since it shows qualitatively the factors which determine the magnitude of the electromotive force. This is illustrated by the following problems, which relate to certain cells of technical importance.

Prob. 52. One form of the Clark standard cell at 20° is represented by the formula: $Zn + ZnSO_4.7H_2O, ZnSO_4.16.8H_2O, Hg_2SO_4 + Hg$. *a.* Specify the exact change of state that occurs when two faradays pass through the cell. *b.* Show that even in an actual cell, with only a finite quantity of solution, no variation of the electromotive force results when two faradays pass, provided the change in state takes place slowly enough.

Prob. 53. The Leclanché cell consists essentially of a zinc rod (amalgamated to diminish local voltaic action) dipping into a concentrated NH_4Cl solution containing $ZnCl_2$, and a carbon rod coated with MnO_2 dipping into the same solution. *a.* Formulate the ion-reaction that takes place at each electrode and the whole reaction in the cell, taking into account the facts that the MnO_2 is reduced to Mn_2O_3,

and that $Zn(OH)_2$ is soluble in NH_4Cl solution. *b.* Show in what direction the electromotive force of the cell would be changed by decreasing the concentration of the NH_4Cl.

Note.—The common "dry cell" is a Leclanché cell to which some porous material, such as paper-pulp or sawdust, has been added to hold the liquid.

Prob. 54. In the nickel-iron (Edison) storage cell, **Fe, KOH(21%), Ni(OH)₃,** the main reaction is **Fe + 2Ni(OH)₃ = Fe(OH)₂ + 2Ni(OH)₂** (the degree of hydration of the three oxides being, however, somewhat indefinite). *a.* Write the ion-reaction occurring at each electrode. *b.* Show in what direction each of the electrode-potentials, and also the electromotive force of the whole cell, would vary with increase of the KOH concentration.

141. Concentration-Changes attending Voltaic Action and the Resulting Polarization.— Throughout the foregoing considerations, as an aid in evaluating the electromotive force, it has been assumed that so large a quantity of solution is present in the cell that only infinitesimal concentration-changes are produced in it by the passage of a finite quantity of electricity. The fact that this is not the case in actual cells must be taken into account.

Prob. 55. The electromotive force E at 15° of the lead storage-cell varies with the mol-fraction x of the H_2SO_4 (for values of x up to 0.10) according to the equation $E = 1.855 + 3.80x - 10x^2$. Out of a certain cell which contains 1300 g. of 10 mol-percent H_2SO_4 a steady current of 5.36 amperes is taken for 10 hours. *a.* Calculate the electromotive force of the cell at the beginning and at the end. *b.* Derive an integral (expressed in terms of molal composition and numerical coefficients) by which the electrical energy producible by the outflow of any given quantity of electricity from any similar lead storage-cell could be calculated.

In practice the electromotive force is often decreased much more than these considerations indicate because the concentration-changes actually occur in the immediate neighborhood of the electrodes and are only gradually distributed by convection or diffusion through the whole body of the solution. Thus in the lead storage-cell water is produced and acid is destroyed by the electrode-reaction in the solution impregnating the porous lead-peroxide electrode, and the acid can only be replenished from the main body of the solution by the slow process of diffusion. This phenomenon is one kind of polarization, sometimes called *concentration-polarization;* the name *polarization* being used in general to denote the production by the passage of the current of any change in the solution adjoining the electrode or in the surface of the electrode which makes its potential deviate from its normal value.

Prob. 56. When a certain current is taken at 25° out of a certain cell of the form **Zn, $ZnSO_4$(1 f.), $CuSO_4$(1 f.), Cu,** the electromotive force soon becomes fairly constant and remains so for a time at a value 0.06 volt below its normal value. *a.* Show quantitatively how this might be accounted for by concentration-polarization. *b.* Explain how the polarization would be affected by increasing the current; by using

smaller electrodes without changing the current, thereby increasing the *current-density*, by which is meant the current in amperes per unit-area (per square centimeter or decimeter) of electrode-surface; and by stirring the solutions, these being separated from each other by a porous cup.

142. Electrolysis in Relation to Applied Electromotive Force.— In order to produce electrolysis in any electrolytic cell there must obviously be applied from an external source an electromotive force at least equal to the electromotive force that is produced by the combination of solution and electrodes, considering it as a voltaic cell. The value of the electromotive force that must be applied to compensate this *back electromotive force* of the cell under the actual conditions, and thus produce appreciable electrolysis, is called the *decomposition-potential*. Its value, when not influenced by indefinite polarization-effects, such as are described in Art. 143, can therefore be calculated by the methods considered in Arts. 130–137. It is important to recognize this fact; for the decomposition-potential is sometimes treated as if it were an essentially independent quantity.

Prob. 57.—Experimental Determination of Decomposition-Potential. —A 0.05 formal solution of $CuSO_4$ is placed at 25° in a certain electrolytic cell between a mercury electrode covered with Hg_2SO_4 and a copper electrode. An external electromotive force is applied at the mercury electrode, first of 0.1, then of 0.2, 0.3, 0.4, 0.5, and 0.6 volt. An ammeter placed in series with the cell shows that no appreciable current passes until 0.4 volt is applied, when the current is 0.8 milliamperes; while with 0.5 volt the current is 2.8 milliamperes, and with 0.6 volt it is 4.8 milliamperes. *a.* Plot these values of the current as ordinates and of the potential as abscissas, and derive from the plot the value of the decomposition-potential. *b.* Calculate the resistance of the solution.

Prob. 58.— Deposition of Metals by Electrolysis.—A solution 0.05 formal in H_2SO_4 and 0.05 formal in $CuSO_4$ is electrolyzed at 25° between a mercury anode and a platinum cathode. In the mixture the salt may be assumed to be 35% ionized and the acid to be 35% ionized into $2H^+$ and $SO_4^=$ and 60% ionized into H^+ and HSO_4^-. *a.* Calculate from the electrode-potentials (taking that of $Hg + Hg_2SO_4$, $SO_4^=(1 m.)$ as —0.62 volt) the minimum electromotive force which would have to be applied in order to cause the copper to deposit. *b.* To what value would this electromotive force have to be increased after 99% of the copper had been precipitated in order that the deposition might continue, assuming

the ionizations to be the same as in the original mixture? *c*. What is the minimum electromotive force at which hydrogen could be continuously set free, assuming that it attains at the cathode an effective pressure of 1 atm.?

   Prob. 59.—Separation of Elements by Electrolysis.—A solution 0.1 normal in KCl, 0.1 normal in KBr, and 0.1 normal in KI is placed, together with a platinum electrode, in a porous cup; and this is placed within a larger vessel containing a zinc electrode and a large quantity of 0.1 normal $ZnCl_2$ solution. Assuming complete ionization of the salts, calculate the applied electromotive force required at 25°, *a*, to liberate 99.9% of the iodine; *b*. to set bromine free at a concentration of 0.0001 molal; *c*, to liberate 99.9% of the bromine (which remains in solution); and *d*, to liberate chlorine at a concentration of 0.0001 molal.

143. Electrolysis in Relation to Polarization.—In electrolysis, as in voltaic action, concentration-changes are produced at the electrodes; and these have the effect of increasing the applied electromotive force required. Thus in electrolyzing a solution of copper sulphate between copper electrodes (as is done in copper plating) only an infinitesimal electromotive force is required to start the deposition; but the solution around the cathode soon becomes less concentrated in copper and the solution around the anode more concentrated in copper, producing a concentration-cell, like those of Art. 131, with an electromotive force opposite to that applied. This back electromotive force can of course be calculated for any given concentration-changes. It would evidently be diminished by decreasing the current-density, by agitating the whole solution, or by rotating the electrodes.

   When a gas, such as hydrogen or oxygen, is set free at an electrode, a phenomenon, known as *gas-polarization,* is observed which does not occur in the deposition of metals. For when a gas is involved in the electrode-reaction its partial pressure determines the electrode-potential. Hence in a cell exposed to the air a slow, continuous electrolysis may take place before the applied electromotive force equals the electromotive force of the cell when the gas-pressure is one atmosphere; for the gas-forming substance is produced on the electrode at a lower pressure and is dissolved in the solution and carried away by convection and diffusion. Moreover, a sudden in-

crease in the rate of electrolysis does not take place when the applied electromotive force is increased beyond that corresponding to a pressure of one atmosphere; for the gas-forming substance then passes into the electrode-surface at this high pressure, producing a supersaturated solid solution from which the gas does not escape rapidly enough to reduce the effective pressure to one atmosphere.* There is therefore a back electromotive force produced by the cell which is larger than its electromotive force when the gas-pressure is one atmosphere. The excess of the one over the other is called the *polarization* or *overvoltage*.

Prob. 60.—Concentration-Polarization.—Calculate the electromotive force of polarization that would result in electrolyzing at 25° a 0.01 formal $CuSO_4$ solution between copper electrodes if the copper-ion concentration became 0.001 formal around the cathode and 0.1 formal around the anode, assuming equal ionization of the salt at these two concentrations.

Prob. 61.—Gas Polarization.—Electromotive forces successively increasing in magnitude were applied at 22° to an electrolytic cell consisting of a large, unpolarizable, platinized platinum plate as anode, a small mercury surface as cathode, and a 0.1 normal H_2SO_4 solution as electrolyte. Hydrogen gas at 1 atm. was bubbled steadily through the cell, and a resistance of 100,000 ohms was placed in series with it, the resistance of the cell being negligible in comparison. The current-strengths I in millionths of an ampere corresponding to various applied electromotive forces E in volts were as follows:

I	0.06	0.44	1.20	2.20	3.70	4.82
E	0.32	0.48	0.62	0.77	0.95	1.08

a. Plot these current-strengths as ordinates against the electromotive forces as abscissas. *b.* Calculate the back electromotive force corre-

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* In some cases the solid solution is probably a solution in the metal of the gas-forming substance itself or of the corresponding monatomic substance (thus of H or O in the case of H_2 or O_2). In other cases there is evidence that it is a solution in the metal of an unstable compound of the metal with the gas-forming substance; thus higher oxides such as PtO_3 and NiO_2 seem to be formed when oxygen is set free on platinum or nickel. Such compounds have a high dissociation-pressure and are therefore equivalent in their effect on the potential to the gas itself at the same high pressure, assuming equilibrium to be attained between them and the electrolyte in the solution.

The slowness with which the gas escapes from these solid solutions may arise in part from the small rate at which the reactions (such as $2H = H_2$, or $2PtO_3 = 2Pt + 3O_2$) take place within the electrode-surface. The rate of escape of the gas is, moreover, doubtless largely determined by surface-tension effects.

sponding to each of these applied electromotive forces, record these values, and plot the current-strengths against them on the same diagram. *c.* Calculate the effective pressure of the hydrogen at the electrode corresponding to the smallest of these back electromotive forces.

The back electromotive force is experimentally determined by the method illustrated in Probs. 57 and 61, or by finding the smallest value of the applied electromotive force at which bubbles form slowly but continuously at the electrode surface (this giving a value corresponding practically to a minimum current-density), or by applying a definite electromotive force to the cell long enough to charge the electrodes with the decomposition-products and then short-circuiting the electrodes through a high-resistance potentiometer, the applied potential being at the same time removed. From this back electromotive force the overvoltage is obtained by subtracting the theoretical electromotive force corresponding to a gas-pressure of one atmosphere.

The overvoltage is always found to increase with increase of the applied electromotive force and of the current-density; but it varies in a highly specific way with the chemical nature of the gas and with the chemical nature and physical state of the metallic electrode. Thus in certain experiments made with 1-normal H_2SO_4 with a low applied potential and low current-density the overvoltage of the hydrogen was found to be zero on a platinized electrode, 0.03 volt on smooth platinum, 0.36 volt on lead, and 0.44 volt on mercury; while with a much higher applied potential and current-density it was found to be 0.07 volt on platinized platinum, 0.65 volt on smooth platinum, 1.23 volts on rough lead, and 1.30 volts on mercury. And in certain experiments with 2-normal KOH with a moderate current-density the overvoltage of the oxygen was found at the start to be 0.44 volt on platinized platinum, 0.84 volt on smooth platinum, and 0.50 volt on iron; the value increasing to 1.46 on smooth platinum and to 0.59 on iron after two hours' passage of the current.

The phenomenon of gas-polarization and the overvoltage attending it are of great significance in technical processes. The overvoltage may greatly diminish the energy-efficiency of the process, the *energy-efficiency* being the ratio of the minimum electrical energy theoretically required to produce a definite quantity of some

product of the electrolysis to the energy actually expended. Overvoltage may also make processes practicable which would otherwise not be possible; thus in charging a lead storage-cell hydrogen is not set free at the lead electrode owing to its overvoltage, although the potential of the half-cell H_2(1 atm.), $H_2SO_4 20H_2O$ is about 0.4 volt less than that of the half-cell **Pb + PbSO$_4$, H$_2$SO$_4$20H$_2$O.**

Prob. 62.—Energy-Efficiency and Overvoltage.—In a certain commercial alkali-chlorine cell sodium hydroxide and chlorine are produced at an iron cathode and graphite anode, respectively, by the continuous electrolysis of a 25% NaCl solution which is slowly flowed through a diaphragm from the anode to the cathode compartment (to prevent hydroxide-ions from migrating to the anode). In practice 4.5 volts are applied to the cell, whose resistance is 0.00080 ohm, yielding a current of 2000 amperes. There flow off each hour from the cathode 27,460 g. of solution containing 10% NaOH and 13% NaCl. The electromotive force of the voltaic cell H_2(1 atm.), NaOH(10%) + NaCl(13%), NaCl(25%), Cl_2(1 atm.) has been independently determined to be 2.3 volts. *a.* Calculate the current-efficiency in the production of the sodium hydroxide. *b.* Calculate the energy-efficiency. *c.* Calculate the overvoltage and the percentage loss in energy-efficiency that arises from it.

144. Review Problems.

Prob. 63. The potential of a platinum electrode in an acid solution of potassium iodate and iodine is found to depend only on the concentrations of H^+, IO_3^-, and I_2. *a.* Write the electrode-reaction attending the passage of ten faradays from the electrode to the solution. *b.* Formulate an expression by which the electrode-potential E at 25° for any small concentrations (H^+), (IO_3^-), (I_2) could be calculated from the electrode-potential E' for the case that $(H^+) = 0.1$, $(IO_3^-) = 0.05$, and $(I_2) = 0.02$ formal.

CHAPTER X

THERMODYNAMIC CHEMISTRY: THE PRODUCTION OF WORK BY CHEMICAL CHANGES AND ITS RELATION TO THEIR EQUILIBRIUM CONDITIONS

FREE–ENERGY CHANGES ATTENDING ISOTHERMAL CHANGES IN STATE

145. Chemical Significance of Free Energy.—It was shown in the preceding chapter that a knowledge of the maximum work produced by isothermal changes in state, or of the corresponding free-energy-decrease attending them, enables the electromotive force of voltaic cells to be evaluated. It will be shown in this chapter that this knowledge also makes possible the determination of the equilibrium-conditions of chemical changes. The development of the principles relating to free energy and the working-out of a complete system of free-energy values are therefore problems of great chemical importance.

The principles determining the free-energy-decrease attending certain kinds of changes have been considered in the preceding chapter. These are summarized in Art. 147. Other principles will be described in later articles. First, however, there will be presented in the next article the conventions adopted in this book for the expression of free-energy values.

146. Conventional Expression of Free-Energy Values.—Little more need be said in regard to the expression of free-energy values than that the same conventions that have already been described in Art. 113 for the expression of heat-effects will be employed for expressing free energies. When necessary, equations expressing changes in free energy may be distinguished from those expressing changes in heat-content by prefixing to them the symbols ($\mathbf{F}$) and ($\mathbf{H}$), respectively; and the absolute temperature may be shown by attaching to this letter a subscript. For example:

$$(\mathbf{F}_{298}) \; H_2(1 \text{ atm.}) \; + \; \tfrac{1}{2}O_2(1 \text{ atm.}) \; = \; H_2O \; + \; 56{,}620 \;\; \text{cal.}$$
$$(\mathbf{H}_{298}) \; H_2(1 \text{ atm.}) \; + \; \tfrac{1}{2}O_2(1 \text{ atm.}) \; = \; H_2O \; + \; 68{,}400 \;\; \text{cal.}$$
$$(\mathbf{F}_{298}) \; H_2O \; = \; -56{,}620 \;\; \text{cal.}$$
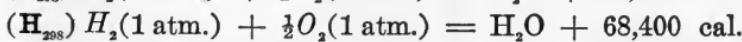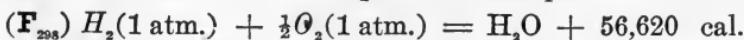
The pressure must always be definite; when not specified, it is

understood to be one atmosphere. Throughout this chapter free-energy values will be expressed in calories on account of their close relations with heat-content data, which are commonly so expressed.

In accordance with the specified convention as to the arbitrary zero-point of the scale, the free energy at any definite temperature of any definite quantity of a substance in any definite state is equal to the free-energy-increase that attends the formation of the substance in that state out of the pure elementary substances at the same temperature, and at a pressure of one atmosphere, each elementary substance being in the state of aggregation that is the stable one at this temperature and pressure. Thus the free energy of $1HI$(1 atm.) refers at 25° to its formation from gaseous hydrogen and solid iodine at one atmosphere; but at 400° it refers to its formation from gaseous hydrogen and gaseous iodine at one atmosphere.

The free energy of a substance in a solution is understood to mean the free-energy-increase attending the formation of the pure substance out of the elementary substances plus that attending the introduction of it into an infinite quantity of the solution under consideration. This free energy is indicated by attaching to the chemical formula in Roman type a parenthesis showing the concentration or composition of the solution; for example, 1KCl(at 0.1 f.), $1H_2SO_4$(in $H_2SO_4 10H_2O$). The free energy of water in a solution is often conveniently referred to that of pure water (instead of to that of hydrogen and oxygen) as zero; and when so referred the symbol N Aq (instead of $N H_2O$) is used; for example, 5Aq (in $H_2SO_4 10H_2O$).

Prob. 1. a. Formulate a free-energy equation for the change in state considered in Prob. 17, Art. 129. *b.* Find the free energy of 1HCl(at 0.1 f.) at 25°. *c.* State what other free-energy change would have to be combined with this one in order to give the free energy at 25° of $1HCl$(1 atm.).

147. Free-Energy Principles Already Considered.—It was shown in Art. 125 that the maximum work (W_R) producible by any isothermal change in state is related to the attendant free-energy-decrease ($-\Delta F$) of the system in the simple way expressed by the equation: $-\Delta F = W_R - \Sigma(\Delta pv)$. It was also shown in Art. 125

that, in order to determine this maximum work or this free-energy-decrease, the change in state must be made to take place reversibly.

It was shown in Art. 126 that the free-energy-decrease attending the change in the pressure from p_1 to p_2 on any substance whose volume is v at the pressure p is given in general by the integral of $v\,dp$ from p_2 to p_1; and that it is given by the expression $-\Delta F = N R T \log(p_1/p_2)$ when the pressure-volume relations of the substance are those of a perfect gas within the pressure-interval involved.

It was also shown in Art. 126 that the free energies of a substance in two different phases are the same when the pressure or concentration is that at which equilibrium prevails.

It was shown in Art. 127 that the free-energy-decrease attending the transfer at the temperature T of N mols of a substance from an infinite quantity of a solution in which its vapor-pressure is p_1 and its concentration is c_1 into an infinite quantity of another solution in which its vapor-pressure is p_2 and its concentration c_2 is given by the expressions:

$$-\Delta F = N R T \log \frac{p_1}{p_2}; \text{ and } -\Delta F = N R T \log \frac{c_1}{c_2}.$$

The first of these expressions holds true whatever the concentrations of the substance, provided its vapor conforms to the perfect-gas law; the second holds true only when the concentrations are so small that the solute conforms to the laws of perfect solutions.

148. The Free Energies of Substances in Their Different Physical States.—The principles summarized in Art. 147 may be applied to the determination of the free energies of a substance in its different physical states, as illustrated by the following problems.

Prob. 2. Calculate the free energy at 25°, a, of I_2(1 atm.); b, of I_2(at 1 m. in H_2O); and c, of I_2(at 1 m. in CCl_4). At 25° the vapor-pressure of pure iodine is 0.305 mm., its solubility in water is 0.00132 molal, and its distribution-ratio between carbon tetrachloride and water is 86.

Prob. 3. a. Describe a process, for each stage of which the free-energy-decrease can be evaluated, by which rhombic sulphur can be converted into monoclinic sulphur, making use of their solubilities in benzene. *b.* From the facts that these solubilities at 25° are 18.2 g. and 23.2 g. per l., respectively, and that the molecular formula of sulphur in

benzene has been shown by molecular-weight determinations to be S_8, calculate the free energy of $1S$ (monoclinic) at 25°. *c.* Predict from the diagram of Art. 95 the conditions under which the free energies of rhombic and monoclinic sulphur are equal.

Prob. 4.—Determination of the Free Energy of a Solute at High Concentration.—a. Formulate a numerical expression by which one may calculate the free energy F_2 of $1NH_3$ (at 8.6 n. in H_2O) from the free energy F_1 of $1NH_3$ (at 0.2 n. in H_2O) with the aid of the values of the distribution-ratio of NH_3 between CCl_4 and H_2O, which are 0.0086 and 0.0040 when the NH_3 concentrations in the water are 8.6 and 0.2 normal, respectively. *b.* State the principles involved. *c.* State how the same free-energy quantity might be obtained from other measurements with the same solutions.

149. Derivation of the Free Energies of Substances from Electromotive Forces.—It was shown in Art. 129 that changes in state can often be caused to take place reversibly in voltaic cells, and that the free-energy-decrease is then given by the expression $-\Delta F = \text{E N F}$, which is valid whatever be the concentrations.

Prob. 5. Calculate the free energy of $1HCl$ (1 atm.) at 25° from the facts that at 25° the cell H_2 (1 atm.), HCl (4 f.), Cl_2 (1 atm.) has an electromotive force of 1.262 volts, and that the vapor-pressure of the HCl in its 4-formal solution is 0.0094 mm.

Prob. 6. Calculate the free energy of $1AgCl$ at 25° from the specific electrode-potentials.

Prob. 7. a. Formulate the free-energy equation which can be derived from the specific electrode-potential of lead, which is $+$ 0.12 volt at 25°. *b.* State what conclusion as to the free energy of lead-ion can be drawn from this value under the conventions that have been adopted.

Prob. 8. Calculate the free energy at 25°, *a*, of $1Cl^-$ (at 1 m.), and *b*, of $1OH^-$ (at 1 m.).

150. The Free-Energy-Decrease attending Isothermal Chemical Changes between Gaseous Substances in Relation to Their Equilibrium Conditions.—It has already been seen in Art. 129 that chemical changes can often be made to take place reversibly in voltaic cells. It will now be shown that there is another kind of reversible process by which they can be brought about. This kind of process, which involves only mechanical work, leads to a relation between the maximum work or free-energy-decrease attending the chemical change and its equilibrium-conditions.

Consider any chemical reaction $aA + bB.. = eE + fF..$ between the gaseous substances A, B,..E, F,..; and consider a change in state which consists in the conversion at the temperature T of a mols of A, b mols of B,.. at pressures p_A', p_B',.. into e mols of E and f mols of F,.. at pressures p_E', p_F'..

To carry out this change in state by a reversible process we make use of an apparatus like that shown in Fig. 11. This apparatus con-
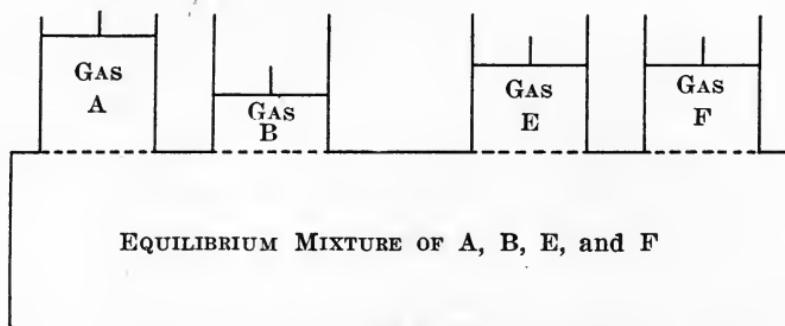

Fig. 11

sists of a reservoir and of a number of cylinders which communicate with it through walls, each of which is permeable for only one of the gases. These walls can be replaced at will by impermeable ones. The cylinders, which serve to hold the separate gases, are provided with weighted frictionless pistons. The reservoir contains a mixture of the gases at any partial pressures p_A, p_B,.. p_E, p_F,.. at which the chemical change is in equilibrium.

Starting now with a mols of A, b mols of B,.. at pressures p_A', p_B'.. in their respective cylinders, consider the following process to be carried out at the temperature T under reversible conditions (always keeping the external pressure on any piston equal within an infinitesimal amount to that of the gas beneath).

1. The cylinders being closed temporarily by impermeable walls, raise or lower the pistons above the gases A, B,.. till the pressures change from p_A', p_B',.. to those, p_A, p_B,.., prevailing in the equilibrium-mixture.

2. Replace the impermeable walls by semipermeable ones, and force the a mols of A, b mols of B,.. into the reservoir, at the same time drawing out into the other cylinders at the pressures p_E, p_F,..

prevailing in the equilibrium-mixture the e mols of E, f mols of F,.. which must form spontaneously out of A, B,.. in order that the equilibrium in the mixture may be maintained.

3. Replace the semipermeable walls under the gases E, F,.. by impermeable ones, and raise or lower the pistons above the gases E, F,.. till the pressures change from the equilibrium-pressures p_E, p_F,.. to the final pressures p_E', p_F'..

By formulating, as is done in Prob. 9, expressions for the free-energy-decrease attending each of the steps in this process and summing up the three values, there is obtained in the case that all the pressures involved are so small that they conform substantially to the perfect-gas law the following expression for the free-energy-decrease attending a chemical change between gaseous substances:

$$- \Delta F = R T \left(\log \frac{p_E{}^e p_F{}^f ..}{p_A{}^a p_B{}^b ..} - \log \frac{p_E'{}^e p_F'{}^f ..}{p_A'{}^a p_B'{}^b ..} \right).$$

Prob. 9.—Derivation and Significance of the Free-Energy Equation. —*a.* Formulate expressions for the free-energy-decrease attending each of the three steps in the process described in the preceding text. *b.* By combining these expressions derive the free-energy equation there given. *c.* State explicitly the change in state to which this equation applies and the difference in the significance of the pressures in the two logarithmic terms; and name a familiar quantity that may be substituted in one of these terms. *d.* Give the form which the equation assumes when the initial and final partial pressures are all unity.

Prob. 10.—Numerical Applications of the Free-Energy Equation. —*a.* Calculate the free-energy-decrease in calories attending the change $2H_2(0.1 \text{ atm.}) + O_2(0.5 \text{ atm.}) = 2H_2O(1 \text{ atm.})$ at $2000°$ from the fact that water-vapor at $2000°$ and 1 atm. is 1.85% dissociated into hydrogen and oxygen. *b.* Calculate also the free energy at $2000°$ of $1H_2O$ (1 atm.), as defined in Art. 146.

Prob. 11.—Derivation of the Mass-Action Law.—Derive the mass-action law expressed in terms of pressures by considering in the derivation of the free-energy equation that the same change in state is brought about by two reversible processes of the type described in the text differing in the respect that different equilibrium-mixtures are contained in the reservoir.

Prob. 12.—Relation of the Free-Energy-Change to the Tendency of the Chemical Change to Take Place.—*a.* Show from the free-energy equation that the substances involved in a chemical change are in equi-

librium when their partial pressures are such that the free-energy-decrease would be zero if the change took place. *b.* Show that in any given mixture the change tends to take place in that direction in which it is attended by a decrease in the free energy.

The conclusion reached in the last problem is another example (see Arts. 126 and 139) of the following general principle: when the conditions of temperature and of pressure or concentration are such that a substance or a group of substances may undergo a change in state without any attendant change in free energy, the two states are in equilibrium with each other. More briefly expressed, the condition $-\Delta F = 0$ is a criterion of equilibrium.

151. The Free-Energy Equation for Chemical Changes between Solutes at Small Concentrations.—It can be shown, as is done in Prob. 13, that the free-energy-decrease attending at the temperature T the chemical change:

$$a\mathrm{A}(\text{at } c_{\mathrm{A}}{}') + b\mathrm{B}(\text{at } c_{\mathrm{B}}{}') \ldots = e\mathrm{E}(\text{at } c_{\mathrm{E}}{}') + f\mathrm{F}(\text{at } c_{\mathrm{F}}{}') \ldots,$$

where A, B,.. E, F,.. are solutes at the small concentrations $c_{\mathrm{A}}{}', c_{\mathrm{B}}{}', \ldots c_{\mathrm{E}}{}', c_{\mathrm{F}}{}' \ldots$, is given by the equation:

$$-\Delta F = R\,T\left(\log \frac{c_{\mathrm{E}}{}^{e}\, c_{\mathrm{F}}{}^{f} \ldots}{c_{\mathrm{A}}{}^{a}\, c_{\mathrm{B}}{}^{b} \ldots} - \log \frac{c_{\mathrm{E}}{}'^{e}\, c_{\mathrm{F}}{}'^{f} \ldots}{c_{\mathrm{A}}{}'^{a}\, c_{\mathrm{B}}{}'^{b} \ldots}\right).$$

In this equation, which is obviously closely analogous to that for gaseous substances, the quantities $c_{\mathrm{A}}, c_{\mathrm{B}}, \ldots c_{\mathrm{E}}, c_{\mathrm{F}}, \ldots$ are any small concentrations at which the substances are in equilibrium.

Prob. 13. Derive the free-energy equation given in the preceding text by considering that all the solutes are volatile and that the change in state is brought about by vaporizing A, B,.. out of their solutions, converting them into E, F,.. in the gaseous state by the process described in the text of Art. 150, and condensing E, F,.. into their solutions; each of these changes being carried out under equilibrium-conditions so that it may be reversible. Represent by $p_{\mathrm{A}}{}', p_{\mathrm{A}}, \ldots p_{\mathrm{E}}{}', p_{\mathrm{E}} \ldots$ the partial vapor-pressures corresponding to the concentrations $c_{\mathrm{A}}{}', c_{\mathrm{A}}, \ldots c_{\mathrm{E}}{}', c_{\mathrm{E}}, \ldots$, and assume that in accordance with Henry's law the pressures and concentrations are proportional.

Prob. 14. Calculate the free-energy-decrease attending the change $\mathrm{NH_4^+}(\text{at } 0.1 \text{ f.}) + \mathrm{CN^-}(\text{at } 0.1 \text{ f.}) = \mathrm{NH_3}(\text{at } 0.1 \text{ f.}) + \mathrm{HCN}(\text{at } 0.1 \text{ f.})$ at 25° from the fact that $\mathrm{NH_4^+CN^-}$ in 0.1 formal solution at 25° is 52% ionized into $\mathrm{NH_4^+}$ and $\mathrm{CN^-}$ and 41% dissociated into $\mathrm{NH_3}$ and HCN.

Although the free-energy equation has been derived above under the assumptions that the solutes are volatile and that their concentrations and vapor-pressures are so small that Henry's law is applicable, it can be shown that this equation (like equation (3) of Art. 127) is valid provided only that the concentrations are so small that the solutes conform to the laws of perfect solutions, for example, to the osmotic-pressure equation $P = c\,R\,T$.

The validity of the mass-action law for solutes at small concentrations can be derived from this free-energy equation just as that for gases at small pressures was derived in Prob. 11 from the free-energy equation of the preceding article. The validity of the mass-action law therefore involves only that of the law of perfect solutions or of perfect gases; and it will hold true when applied to any definite chemical change with a degree of exactness corresponding to that with which the substances involved conform under the given conditions of concentration or pressure to the law of perfect solutions or of perfect gases.

152. The Free-Energy Equations for Chemical Changes between Solid Substances and Gaseous or Dissolved Substances at Small Concentrations.—When pure solid substances are involved in a chemical change with gaseous or dissolved substances it is not necessary to include in the free-energy equation their pressures or concentrations; for these would obviously have the same value (that of the vapor-pressure or solubility of the solid) in the two logarithmic terms corresponding to the equilibrium conditions and the initial and final conditions, respectively. The same is true of the pressure of a pure liquid when it is involved in a chemical change with gaseous substances that are not much soluble in it, as in the formation of liquid water from hydrogen and oxygen.

*Prob. 15.* Calculate from the data of Prob. 47, Art. 91, the free-energy-decrease attending at 25° the chemical change:
$$NH_4SH = NH_3 (1\,atm.) + H_2S (1\,atm.).$$
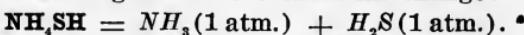
Prob. 16. Calculate the free energy of $1Ag_2O$ at 25° from the fact that its dissociation-pressure at 25° is 0.38 mm.

Prob. 17. Calculate from the data of Prob. 59, Art. 93, the free-energy-decrease attending at 25° the chemical change:
$$AgSCN + Br^- (0.1\,f.) = AgBr + SCN^- (0.1\,f.).$$

153. Calculation of the Equilibrium-Constants of Chemical Changes and of the Electromotive Forces of Voltaic Cells from the Free Energies of the Substances Involved.—When the values of the free energies of substances have been once determined by the methods already described, these values can be employed, conversely, for calculating the equilibrium-constants of chemical changes and the electromotive force of voltaic cells in which the substances are involved. From this fact arises the great importance, referred to in Art. 145, of a systematic knowledge of free-energy values.

Prob. 18. a. Calculate from the free-energy values already considered the equilibrium-constant at 25° of the reaction:

$$Ag_2O + H_2O + 2Cl^- = 2AgCl + 2OH^-.$$
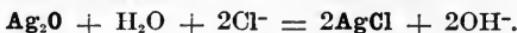
b. State what mixture would finally result if $1Ag_2O$ were treated at 25° with 1 l. of 0.1 normal NaCl solution.

Prob. 19. a. Calculate from the free-energy values the equilibrium-constant of the reaction $4HCl + O_2 = 2Cl_2 + 2H_2O$ at 25°. *b.* Calculate the mol-fractions of chlorine and oxygen in the gas which at 1 atm. and 25° would escape from a 4-formal HCl solution if oxygen at 1 atm. were passed through it in contact with a catalytic agent so that equilibrium was established. At 25° in 4-formal HCl solution the vapor-pressures of the water and HCl are 19.6 mm. and 0.0094 mm., respectively.

Prob. 20. Calculate from the free-energy values and the other data needed the electromotive forces at 25° of the following cells:

a. H_2(1 atm.), H_2SO_4(0.01 f.), O_2(1 atm.).

b. Cl_2(1 atm.), HCl(4 f.), O_2(1 atm.).

154. Derivation from the Second Law of Energetics of an Expression for the Quantity of Work that can be produced when a Quantity of Heat passes from One Temperature to Another.—The remainder of this chapter is devoted to a consideration of the effect of temperature on the free-energy-changes that attend isothermal changes in state. To this effect is closely related, in virtue of the free-energy relations already derived, the effects of temperature on the electromotive force of voltaic cells and on the equilibrium of chemical changes. But before these effects can be properly considered the more general thermodynamic relation referred to in the title of this article must be known. This will now be derived.

It has been already stated (in Art. 124) that, when a quantity of heat is transformed into work by a *cyclical process* (that is, by a process in which the system undergoes no permanent change in state), an additional quantity of heat is always taken up from surroundings at a higher temperature and given out to surroundings at a lower temperature. That is to say, even when a difference of temperature exists, only a fraction of the heat taken up by the system from the warmer surroundings can be transformed into work. Important questions at once arise as to what determines the fraction that can be so transformed—as to whether it is dependent on the nature of the process employed, and how it varies with the temperatures.

In order to determine whether the quantity of work that can be produced when any definite quantity of heat is transferred by a cyclical process from a higher to a lower temperature is dependent upon the nature of the system employed for the transformation, or upon the way in which the transformation is carried out, let us assume that two different reversible cyclical processes, carried out with different systems or in a different way with the same system, could produce two unequal quantities of work by transferring an equal quantity of heat from a higher to a lower temperature. Let us then cause the process that produces the larger quantity of work W'' to take place in such a way that it takes up a quantity of heat Q_1 at the higher temperature T_1, transfers a part of it Q_2 to

the lower temperature T_2, and transforms the remainder into work W''; and let us cause the other process, which in transferring the same quantity of heat Q_2 from T_1 to T_2 produces the smaller amount of work W', to take place in the reverse direction—that is, so that it takes up the heat Q_2 transferred by the former process to the lower temperature, and raises it to the higher temperature by expending the required amount of work W'. It is then evident that the net result of these operations would be the production of a quantity of work $W'' - W'$ from an equivalent quantity of heat without any other change having been brought about either in the systems or in the surroundings. Since this is contrary to the fundamental statement of the Second Law, the supposition made that the two processes produce unequal quantities of work is untenable. This important conclusion may be explicitly stated as follows: the maximum amount of work which can be produced when a definite quantity of heat is transferred from one temperature to another by any process in which the system employed undergoes no permanent change in state is not dependent on the nature of the process.

By the conclusion just reached the determination of the relation between the temperatures and the proportion of heat transformable into work is greatly facilitated; for evidently it is now only necessary to determine what that relation is for a single reversible cyclical process. Such a process is considered in the following problem.

Prob. 21. With N mols of a perfect gas contained in a cylinder closed with a weighted frictionless piston and having a volume v_1 and temperature T the following process, consisting of four distinct parts, is carried out reversibly: (1) The gas is placed in a large heat-reservoir at the temperature T; and, by gradually diminishing the weight on the piston, it is caused to expand until its volume becomes v_2. (2) The piston is fixed so that the volume must remain constant, and the gas is placed in a large heat-reservoir at a temperature $T + dT$. (3) Keeping the gas in the heat-reservoir at the temperature $T + dT$, it is compressed by releasing the piston and gradually increasing the weight upon it until the volume v_2 of the gas has been restored to its original value v_1. (4) The piston is again fixed so as to keep the volume constant, and the gas is placed in a heat-reservoir at the temperature T. *a.* Formulate an expression for the quantities of work W_1, W_2,.. produced in the surroundings and for the quantities of heat Q_1, Q_2,.. withdrawn from them in the separate steps of this process.

b. Formulate a relation between the quantity of work ΣW produced in the whole process and the quantity of heat Q withdrawn from the reservoir at the temperature T.

Since it has been shown that the Second Law requires that the same quantity of work be produced when a definite quantity of heat is transferred by any reversible cyclical process whatever from one definite temperature to another, it is evident that the equation derived in the preceding problem for one such process is an exact expression of the Second Law for every such process. This equation therefore expresses one of the fundamental principles of physical science.

The equation just derived, which will be called simply the *second-law equation*, may, to show its significance most clearly, be written in the form:

$$\Sigma W = -\, Q\, \frac{dT}{T}.$$

In this equation ΣW denotes the algebraic sum of all the quantities of work produced in any reversible cyclical process taking place at two temperatures T and $T + dT$ in which the quantity of heat Q is withdrawn from the surroundings at the temperature T; the quantity of this heat not transformed into work being imparted to the surroundings at $T + dT$. The work-quantity ΣW is obviously infinitesimal in correspondence with the infinitesimal temperature-difference dT.

Prob. 22. Show that the second-law equation leads to the following special conclusions: *a.* When there is no difference of temperature in the surroundings heat cannot be transformed at all into work by any cyclical process. *b.* In order to carry heat from a lower to a higher temperature work must be withdrawn from the surroundings. *c.* The fraction of the heat transformable into work for a given difference in temperature is greater the lower the temperature. *d.* When the higher temperature is only infinitesimally greater than the absolute zero heat can be completely transformed into work.

EFFECT OF TEMPERATURE ON CHEMICAL EQUILIBRIUM AND ELECTROMOTIVE FORCE

155. Effect of Temperature on the Pressure at which the Phases of Univariant Systems are in Equilibrium. — An important relation derivable from the second law of energetics is that named in the title of this article. It is expressed by the following equation, known as the *Clapeyron equation:*

$$\frac{dp}{dT} = \frac{1}{T}\frac{\Delta H}{\Delta v}.$$

In this equation dp denotes the increase produced by a temperature-increase dT in the pressure at which the phases of a univariant system (like one consisting of ice and water, or of $CaCO_3$, CaO, and CO_2) are in equilibrium at the temperature T, and ΔH and Δv denote the increases in heat-content and in volume which attend the conversion at the temperature T and at the equilibrium-pressure p of any definite quantity of one phase or set of phases into another phase or set of phases.

This equation can be derived from the second-law equation in the way shown in the following problem.

Prob. 23. Derive the Clapeyron equation from the second-law equation by considering the quantities of work and heat involved in the following cyclical process: Starting with some definite quantity of a substance (for example, $1H_2O$) existing in a phase (for example, liquid water) which is in equilibrium with a second phase (for example, ice) at the temperature T and pressure p, cause it to pass under these equilibrium conditions from the first phase in which its volume is v_1 into the second phase in which its volume is v_2; then heat the second phase to $T + dT$, whereby the pressure becomes $p + dp$ and the volume $v_2 + dv_2$; now cause it to go over into the first phase at $T + dT$ under the equilibrium pressure $p + dp$, whereby the volume becomes $v_1 + dv_1$; and finally cool this first phase to T, whereby it reverts to its original condition.

In applications of the Clapeyron equation a definite change in state should first be formulated, and then ΔH and Δv should be evaluated in accordance with it, expressing the heat-quantity ΔH and the work-quantity $dp \cdot \Delta v$ in the same units. When one of the phases involved is a gas at small pressure, Δv may be determined by neglecting the volume of the solid or liquid phases and expressing the volume of

the gaseous phase in terms of its temperature and pressure with the aid of the perfect-gas law. Applications of the equation to systems of this kind (those involving liquid and gaseous phases) were considered in Art. 22. Other applications are illustrated by the following problems.

Prob. 24. Derive from the Clapeyron equation a principle expressing the direction of the effect of pressure on the melting-point of solid substances, taking into account the fact that fusion is always attended by an absorption of heat.

Prob. 25. Calculate the variation per atmosphere of the melting-point of ice. At 0° and 1 atm. its density is 0.917 and the heat of fusion of 1 g. is 79.7 cal.

Prob. 26. a. Calculate the variation per atmosphere of the transition-temperature (95.0°) of rhombic into monoclinic sulphur from the densities of the two forms, which are 2.07 and 1.96 respectively, and from the fact that the transition of 1 at. wt. of sulphur from the rhombic into the monoclinic form is attended at 95° by an absorption of 105 cal. *b.* What does this show as to the slope of the line BE in the sulphur diagram shown in Fig. 7, Art. 95? and what conclusion as to the slope of the line CF can be drawn by considering the value of the density of liquid sulphur, which is 1.81 at 115°?

Prob. 27. With the aid of the temperature–vapor-pressure curves of Fig. 8 in Art. 101 derive approximate values of the heat-effect attending the reaction $Na_2HPO_47H_2O + 5H_2O = Na_2HPO_412H_2O$ at 25°.

In order to integrate the Clapeyron equation exactly, ΔH and Δv must be expressed as functions of the equilibrium-temperature or of the equilibrium-pressure. When the system consists of only solid and liquid phases and when only moderate changes of pressure (such as 20 atm.) are involved, ΔH, Δv, and T in the second member of the equation may be considered constant in approximate calculations. When one of the phases consists of a perfect gas, Δv may be expressed as a temperature-function by means of the perfect-gas equation. The heat-quantity ΔH may always be so expressed in terms of the heat-capacities of the substances involved, in the way described in Art. 115.

Prob. 28. Calculate the melting-point of ice at 11 atm. with the aid of the data of Prob. 25.

Prob. 29. State what heat-quantity can be calculated from the dissociation-pressures of NH_4SH into NH_3 and H_2S, which are 500 mm. at 25° and 182 mm. at 10°; and formulate a numerical expression by which it can be calculated, assuming it to be constant through the temperature interval involved.

Prob. 30. Calculate the vapor-pressure of solid iodine at 25° from the following data: its vapor-pressure at 100° is 47.5 mm., its molal heat of vaporization at 100° is 14,600 cal., its atomic heat-capacity is 6.7 between 25° and 100°, and the molal heat-capacity of its vapor at constant pressure is 7.8 between those temperatures.

The derivation of the Clapeyron equation shows that it determines the equilibrium-conditions of any type of system in which an isothermal change in state can take place under a constant equilibrium-pressure which is determined only by the temperature; for evidently in all such cases, and only in such cases, will the work-quantities involved in the cyclical process by which the equation was derived have the found values. In other words, the equation is applicable to all systems, and only to systems, of the univariant type or of a type which has become in effect univariant by the specification that the composition of the phases present shall remain constant when the isothermal change in state takes place and when the temperature of the system is varied. Cases of the latter type are illustrated by the following problem.

Prob. 31. a. In applying the Clapeyron equation to determine the effect of temperature on the vapor-pressure of a 10% NaCl solution, specify the change in state to which the quantities ΔH and Δv would correspond. *b.* State what equilibrium could be studied by applying the Clapeyron equation to a system consisting of solid sodium chloride and its saturated solution, and specify the change in state to which the quantities ΔH and Δv would correspond.

156. Fundamental Equation expressing the Effect of Temperature on the Free-Energy-Changes attending Isothermal Changes in State.

Prob. 32. A certain reversible cyclical process involves the following steps: (1) Any change in state of any system at the temperature T, by which a quantity of work W is produced; (2) a change in the temperature of the system at constant volume from T to $T + dT$; (3) a change in the state of the system at the temperature $T + dT$ which is the reverse of the change in state in the first step, this change being attended by a production of a quantity of work $-(W + dW)$; (4) a change in the temperature of the system at constant volume from $T + dT$ to T. *a.* Find an expression for ΣW for this process. *b.* By substituting it in the second-law equation and by making other appropriate substitutions show that the change $d(-\Delta A)$ with the temperature of the decrease in work-content attending any isothermal change in state is expressed by the equation

$$\frac{(d - \Delta A)}{dT} = \frac{\Delta U - \Delta A}{T},$$

in which ΔU represents the change in the energy-content of the system attending the change in its state at the temperature T.

Prob. 33. A certain reversible cyclical process involves the same steps as the process described in Prob. 23 except that the system during the changes in temperature in steps (2) and (4) is kept at constant pressure, instead of at constant volume. *a.* Find an expression for ΣW for this process, representing the pressures and volumes of the system at the beginning of each of the four steps by (1) p_1 and v_1; (2) p_2 and v_2; (3) p_2 and $v_2 + dv_2$; and (4) p_1 and $v_1 + dv_1$. *b.* By substituting this expression in the second-law equation and making other appropriate substitutions based on the definitions of $-\Delta F$ and ΔH given in Arts. 125 and 112, show that the change $d(-\Delta F)$ with the temperature of the free-energy-decrease attending any isothermal change in state is expressed by the equation

$$\frac{d(-\Delta F)}{dT} = \frac{\Delta H - \Delta F}{T}$$

in which ΔH represents the change in the heat-content of the system attending the change in its state at the temperature T.

The equations derived in the preceding problems:

$$\frac{d(-\Delta A)}{dT} = \frac{\Delta U - \Delta A}{T} \quad \text{and} \quad \frac{d(-\Delta F)}{dT} = \frac{\Delta H - \Delta F}{T}$$

are fundamental expressions of the Second Law in the form most suitable for physico-chemical applications. It is important fully to appreciate the significance of the quantities occurring in them and the condition under which each equation is applicable. The quantities $-\Delta A$ and $-\Delta F$ denote the decreases in the work-content and in the free-energy-content of the system which attend any isothermal change in its state at the temperature T; and ΔU and ΔH denote the accompanying increases in its energy-content and heat-content. The differential quantities $d(-\Delta A)$ and $d(-\Delta F)$ signify that when the same change in state takes place at $T + dT$, instead of at T, it is attended by a work-content-decrease of $-(\Delta A + d(\Delta A))$ and by a free-energy-decrease of $-(\Delta F + d(\Delta F))$, instead of one of $-\Delta A$ and of $-\Delta F$. The work-content equation is applicable to cases where the initial volume, and also the final volume, of the system is the same at the two temperatures; and the free-energy equation is applicable to cases where the initial pressure, and also the final pressure, is the same at the two temperatures.

Throughout the following considerations only the free-energy equation will be employed. For purposes of integration this equation is more conveniently written in the following forms:

$$d\left(\frac{-\Delta F}{T}\right) = \frac{\Delta H}{T^2} dT; \text{ or } \frac{-\Delta F_2}{T_2} - \frac{-\Delta F_1}{T_1} = \int_{T_1}^{T_2} \frac{\Delta H}{T^2} dT.$$

This equation in any of its forms will be called the *second-law free-energy equation.*

Prob. 34. Show that the two differential forms of the free-energy equation are identical by carrying out in the first member of the second one the indicated differentiation and by making other simple transformations.

157. The Effect of Temperature on the Electromotive Force of Voltaic Cells.—By substituting in the second-law free-energy equation just derived the expressions previously obtained (in Arts. 126, 127, 129, and 150–152) for the free-energy-decrease attending different changes in state more specific relations expressing the effect of temperature result. Thus by substituting for $-\Delta F$ the value E N F, **the** following expression, known as the *Gibbs-Helmholtz equation,* for the effect of temperature on the electromotive force of voltaic cells is obtained:

$$\text{N F} \frac{d\text{E}}{dT} = \frac{\Delta H + \text{E N F}}{T}; \text{ or } \text{N F} \, d\left(\frac{\text{E}}{T}\right) = \frac{\Delta H}{T^2} dT.$$

In this equation ΔH denotes the increase in heat-content which attends the change in state that takes place when N faradays of electricity flow through a cell of electromotive force E containing infinite quantities of the constituent substances.

Prob. 35. Show from the Gibbs-Helmholtz equation under what conditions the electromotive force of a cell, *a,* is independent of the temperature; *b,* is proportional to the absolute temperature; *c,* increases with rising temperature; *d,* decreases with rising temperature.

Prob. 36. *a.* Calculate the temperature-coefficient at 25° of the electromotive force of the cell H_2(1 atm.), H_2SO_4(0.01 f.), O_2(1 atm.). *b.* Calculate the electromotive force of this cell at 0°, assuming that the heat-effect attending the change in state does not vary appreciably between 0 and 25°.

Prob. 37. Calculate the temperature-coefficient at 25° of the electromotive force (1.262 volts) of the cell H_2(1 atm.), HCl(4 f.), Cl_2(1 atm.)

from the heat of formation of $1HCl$ (—22,000 cal.) and its heat of solution (given in Art. 121).

Prob. 38. *a.* State what heat data would be needed to calculate accurately the temperature-coefficient of the specific electrode-potential of zinc at 25°. *b.* Calculate its value, referring to Art. 121 for the heat data.

Prob. 39. Calculate the electromotive force at 40° of the storage-cell $Pb + PbSO_4$, $H_2SO_410H_2O$, $PbSO_4 + PbO_2$, from its electromotive force (2.096 volts) at 0° and the heat data needed. The heat-contents at 18° of $1PbSO_4$, $1PbO_2$, and $1H_2SO_4$ are —216,210 cal., —62,900 cal., and —192,900 cal., respectively. For the heat data relating to sulphuric acid solutions see Probs. 41 and 43 of Art. 121. Assume that the change in the heat-content of the cell does not vary between 0 and 40°.

Prob. 40. The electromotive force at the temperature t of the Clark cell, $Zn + ZnSO_47H_2O$, $ZnSO_416.8H_2O$, $Hg_2SO_4 + Hg$, has been very accurately measured and found to be $1.4325 - 0.00119(t - 15) - 0.000007(t - 15)^2$ volts. · *a.* Calculate the change in the heat-content of the cell when two faradays flow through it at 20°. *b.* Considering as in Prob. 52, Art. 140, the change in state that takes place in it, calculate the change in the heat-content from the following thermochemical equations:

$$2Hg + S + 2O_2 = Hg_2SO_4 + 175,000 \text{ cal.}$$
$$Zn + S + 2O_2 = ZnSO_4 + 230,090 \text{ cal.}$$
$$ZnSO_4 + 7H_2O = ZnSO_47H_2O + 22,690 \text{ cal.}$$
$$ZnSO_47H_2O = ZnSO_47H_2O \text{ (in } ZnSO_416.8H_2O) - 4,700 \text{ cal.}$$
$$H_2O = H_2O \text{(in } ZnSO_416.8H_2O) + 50 \text{ cal.}$$
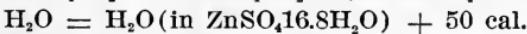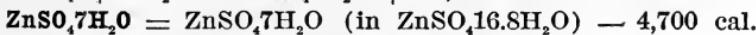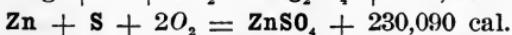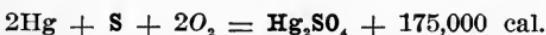
Prob. 41. The electromotive force of the cell $Hg + Hg_2Cl_2$, $KCl(0.01 \text{ f.}) + KNO_3(1 \text{ f.})$, $KNO_3(1 \text{ f.}) + KOH(0.01 \text{ f.})$, $Hg_2O + Hg$ at 0° is 0.1483 volt and at 18.5° is 0.1636 volt. Formulate the change in state that takes place in the cell when two faradays pass through it; and calculate the attendant increase in its heat-content.

158. Comparison of the Electrical Work Producible by Voltaic Cells and the Change in Their Heat-Content.— The two laws of thermodynamics do not show that there is any relation between the value of the decrease of free energy and the value of the decrease of heat-content attending any change in state; for, though the difference between these two values is by the second-law free-energy equation brought into relation with the temperature-coefficient of the free-energy-decrease, this temperature-coefficient may have any magnitude whatever. The two quantities, $-\Delta F$ and $-\Delta H$, are therefore two thermodynamically independent constants, related to the second law and to the first law respectively, each of which is determined solely by the change in state.

Correspondingly there is no definite relation between the electrical work producible by a voltaic cell and the change in its heat-content. It is necessary to emphasize this fact, since it was earlier believed that the two quantities were at least approximately equal, and that the electromotive force of voltaic cells could therefore be satisfactorily calculated under this assumption. This erroneous assumption, which is called Thomson's rule, is expressed by the equation $-\Delta H = \text{E N F}$.

Prob. 42. a. Tabulate beside one another the decreases in heat-content and in free energy which take place when two faradays pass through each of the cells considered in Probs. 39, 40, and 41. Include in the table also the cell $\text{Cu, CuAc}_2\text{100H}_2\text{O, PbAc}_2\text{100H}_2\text{O, Pb}$, which at $0°$ has an electromotive force 0.476 volt and which undergoes a decrease in heat-content of 8770 cal. per faraday. *b.* State the characteristic feature of each of these four cells with respect to the two energy-effects.

Prob. 43. Heat-Effects Attending Voltaic Action.— a. Formulate the heat-effects that occur in the surroundings when two faradays pass through each of the cells named in Prob. 42, assuming that the heat-effect arising from the resistance is negligible. *b.* State qualitatively what temperature-change would occur in each cell if it were heat-insulated from the surroundings.

159. Effect of Temperature on the Equilibrium of Chemical Changes involving Gaseous Substances at Small Pressures.— By substituting in the second-law free-energy equation given at the end of Art. 156 the expression derived in Arts. 150 and 152 for the free-energy-decrease attending an isothermal chemical change between gaseous substances, or between solid and gaseous substances, at small pressures, and noting that the initial and final pressures occurring in this expression must not vary with the temperature if the second-law free-energy equation is to be applicable, there is obtained the following equation, commonly called the *van't Hoff equation,* expressing the effect of temperature on the equilibrium-constant K of the chemical change:

$$d \log \frac{p_{\text{E}}^{e} \; p_{\text{F}}^{f} \cdot \cdot}{p_{\text{A}}^{a} \; p_{\text{B}}^{b} \cdot \cdot} = d \log K = \frac{\Delta H}{R \; T^2} \, dT.$$

Prob. 44. Derive the van't Hoff equation in the way indicated in the preceding text.

Direction of the Effect of Temperature.—

Prob. 45. Derive from the van't Hoff equation a principle expressing a relation between the direction in which an equilibrium is displaced by

increase in temperature and the sign of the change in heat-content attending the reaction.

Prob. 46. a. Show how the equilibrium in a gaseous mixture of Cl_2, HCl, O_2, and H_2O at 25° would be displaced by increasing the temperature. The heat of formation at 25° of $1HCl$ is —22,000 cal. and that of $1H_2O$ is —57,800 cal. *b.* The dissociation-pressure of $CaCO_3$ (and of all other substances which dissociate into one or more gaseous products) increases with rising temperature. State whether heat is absorbed or evolved when the dissociation takes place at constant temperature.

In order to integrate the van't Hoff equation, the heat-content-increase ΔH must be expressed as a function of the temperature. When the heat of the reaction has been measured at a series of temperatures, this function can be derived directly from the results of the measurements. In most cases, however, the temperature-function is obtained from a knowledge of the heat-content-increase at some one temperature and of the heat-capacities at constant pressure of the substances involved in the reaction, with the aid of the expression $d(\Delta H) = \Delta C \cdot dT$, in which ΔC represents the difference between the heat-capacity (equal to $C_E + C_F \cdot \cdot$) of the system in its final state and its heat-capacity (equal to $C_A + C_B \cdot \cdot$) in its initial state. To it corresponds the partially integrated equation

$$\Delta H = \Delta H_0 + \int \Delta C \ dT,$$

in which ΔH_0 is an integration-constant. To complete the integration ΔC must evidently be expressed as a function of the temperature.

Prob. 47. a. Derive the expression $d(\Delta H) = \Delta C \cdot dT$ as described in Art. 115. *b.* Integrate it for the case that ΔC is a function of the form $\Delta C = \Delta C_0 + aT + \beta T^2$, where ΔC_0, a, and β are constants. *c.* Show how a corresponding numerical expression for ΔH for the reaction $2CO + O_2 = 2CO_2$ can be obtained from the heat-capacity data given in Art. 118 and the heats of formation of $1CO$ and $1CO_2$ at 20°, which are —29,000 and —97,000 respectively.

Prob. 48. Integrate the van't Hoff equation between the limits T_1 and T_2, K_1 and K_2, for the following cases: *a,* when ΔC is zero and therefore ΔH does not vary with the temperature; *b,* when ΔC does not vary with the temperature; *c,* when ΔC varies with the temperature in the way stated in Prob. 47.

In numerical applications of the van't Hoff equation, in order to guard against errors in the sign of the heat-content-increase and in its value with respect to the multiple chosen, the reaction under consideration should first be formulated in a definite chemical equation,

and then values of K, ΔH, and ΔC should be adopted in conformity with it. For the heat-capacities of the more important gaseous substances and of elementary solid substances see Arts. 118 and 120.

Prob. 49. It has been found that when dry air (consisting of 21.0 molpercent of oxygen, 78.1 molpercent of nitrogen, and 0.9 molpercent of argon) is kept at 1957° till equilibrium is reached, 4.3% of the oxygen present is converted into nitric oxide. Calculate the molpercent that would be so converted at 3000°. The formation of $1NO$ from its elements at 20° is attended by a heat-absorption of 21,600 cal.

Prob. 50. The dissociation-pressure of **HgO** (into mercury and oxygen gases) at 390° is 180 mm. Calculate its dissociation-pressure at 480°. The heat of formation of **1HgO** at 20° is —21,700 cal. The vaporization of 1Hg at its boiling-point (357°) absorbs 14,160 cal. The mean value of the atomic heat-capacity of liquid mercury between 20° and 357° is 6.36 cal. per degree; and the heat-capacity of **1HgO** is 10.87 at all temperatures. Assume as a sufficient approximation that the heat-capacity of oxygen is constant at its mean value between 20° and 480°.

Prob. 51. Formulate an exact numerical expression by which the dissociation γ of carbon dioxide into carbon monoxide and oxygen at any temperature T and any total pressure p can be calculated. Its dissociation at 1205° and 1 atm. is 0.032%. The heats of formation at 20° of $1CO$ and $1CO_2$ are —29,000 and —97,000 cal.

Prob. 52. When a mixture of 0.49 mol O_2 and 1.00 mol HCl is kept at 386° and 1 atm. in contact with solid cuprous chloride (which acts as a catalyzer) till equilibrium is reached, 80% of the HCl is converted into Cl_2. *a.* Formulate a numerical expression for calculating the equilibrium-constant. *b.* Formulate a numerical expression for calculating the free-energy-decrease attending some specified change in state involving each of the substances at a partial pressure of 1 atm. *c.* Formulate as a function of the absolute temperature the increase in heat-content attending this change in state, using the heat-capacity data given in Art. 118 and the heat-content data given in Prob. 46. *d.* Derive from these results a numerical expression for calculating the equilibrium-constant at 25° of the reaction between $O_2 + 4HCl = 2Cl_2 + 2H_2O$.

160. Effect of Temperature on the Equilibrium of Chemical Changes involving Solutes at Small Concentrations.—By substituting in the second-law free-energy equation the logarithmic concentration expression for the free-energy-decrease attending chemical changes between solutes at small concentrations given in Art. 151, and noting that the last term in that expression (containing the initial and final molal concentrations) does not vary with the temperature, we get

again the van't Hoff equation, now expressed in terms of the equilibrium-concentrations:

$$d \log \frac{c_{\text{E}}^{e} \; c_{\text{F}}^{f} \cdot \cdot}{c_{\text{A}}^{a} \; c_{\text{B}}^{b} \cdot \cdot} = d \log K = \frac{\Delta H}{R \, T^2} \, dT.$$

This equation is applicable also to chemical changes between solid substances and solutes at small concentrations, since it was shown in Art. 152 that the participation of solid substances in the change does not affect the free-energy expression. It applies also to changes in which the solvent (thus the water in aqueous solutions) enters into reaction with solutes at small concentrations.

From the equation, as from the corresponding one in terms of pressures, can be derived the important qualitative principle that the equilibrium of a chemical change is displaced by increase of temperature in that direction in which the reaction is attended by an increase in heat-content (or by an absorption of heat).

The integration of the equation evidently involves the expression of the heat-content as a function of the temperature. Since in the case of solutions the temperature-interval often is not large, the increase in heat-content can frequently be regarded as constant; and it is to be so regarded in the following problems unless otherwise stated. When this is not admissible its variation with the temperature must be known. This must usually be derived from direct determinations of the heat-effects attending the reaction at two or more different temperatures; for there is likely to be a large error involved in calculating it from the partial heat-capacities of the solutes, since they form only a small part of the total heat-capacity of the solution.

Prob. 53. State the conclusions in regard to heats of solution that can be drawn from the facts that the solubility of all gaseous substances is decreased, and that of most solid substances is increased, by an increase of temperature.

Prob. 54. The neutralization of largely ionized univalent acids and bases in fairly dilute solution has been found by direct measurements at 2°, 10°, 18°, 26°, and 34° to evolve $14,750 - 52t$ cal. at the temperature t. The value of the ionization-constant of water at 25° is 0.8×10^{-14}. Calculate its value at 0°.

Prob. 55. Calculate the hydrolysis at 0° of $NH_4^+CN^-$ from the data of Prob. 14 and from the fact that on mixing at 25.00° a solution con-

taining 0.2 NH_3 and 1000 g. water with one containing 0.2 HCN and 1000 g. water and bringing the mixture back to 25.00° there is a heat-evolution of 152 cal., taking into account the fact that the heat of ionization of largely ionizing substances like NH_4CN is approximately zero.

Prob. 56. The solubility of silver chloride in water is 1.10×10^{-5} formal at 20° and 15.2×10^{-5} formal at 100°. *a.* State what heat-quantity can be computed from these data, and calculate its value. *b.* State by what thermochemical measurement it could be determined experimentally.

Prob. 57. The solubility of potassium perchlorate is 0.0781 normal at 10° and 0.1800 formal at 30°, and the ionization (derived from the conductance-ratio) in the saturated solution is 0.823 at 10° and 0.764 at 30°. *a.* State what heat-quantity can be derived from these data, and compute its value. *b.* State in what respect this quantity differs theoretically from the heat of solution ($+$ 12,130 cal.) which has been thermochemically determined by dissolving at 20° $1KClO_4$ in enough water to form with it a saturated solution.

161. Derivation of Free-Energy Values at One Temperature from Those at Another Temperature.—The second-law free-energy equation

$$d \left(\frac{-\Delta T}{T} \right) = \frac{\Delta H}{T^2} \, dT$$

has over the more specialized Gibbs-Helmholtz and van't Hoff equations derived from it the advantage that there can be substituted in it values of the free-energy-decrease obtained from different sources—from the electromotive force of a cell in which the change in state under consideration takes place, from the equilibrium conditions of that change, or from the free energies of the separate substances involved in it. It thus enables an equilibrium-constant at one temperature to be calculated from an electromotive force at another temperature, or the reverse; and it enables either of these to be calculated at one temperature from the free energies of the involved substances at another temperature, or the free energies themselves to be calculated over from one temperature to another—provided always that the necessary heat data are available. It differs furthermore from the van't Hoff equation in the respect that it is not limited to small pressures or concentrations.

Prob. 58. Calculate the free energy of $1HCl$ at 1 atm. and 1200° and its percentage decomposition into hydrogen and chlorine at 1200° from the data of Probs. 5 and 37 and the heat-capacity data of Art. 118.

Prob. 59. Show how the equilibrium-constant of the reaction $H_2S + I_2 = S$ (rhombic) $+ 2H^+I^-$ in dilute aqueous solution at 25° can be calculated from the dissociation at 90° of H_2S (into H_2 and S), from the specific electrode-potentials at 25°, and from such other data as are needed.

Prob. 60. Calculate the free energy at 25° of 1 at. wt. of monoclinic sulphur from the facts that its conversion into rhombic sulphur at its transition-point (95.0°) is attended by a heat-evolution of 105 cal., and that the atomic heat-capacities of the monoclinic and rhombic forms are 6.0 and 5.7 cal. per degree. Tabulate beside this result that obtained in Prob. 3.